Reviewers' comments:

Reviewer #1 (Remarks to the Author):

Please see the pdf attached. 

Reviewer #2 (Remarks to the Author):

The work of Ito et al. aims to analyze the temperature and magnetic field dependent conductivity as a function of gate voltage in ion gel gated semicrystalline PBTTT films. The claim is an understanding of the complex evolution from metallic to strongly localized transport as a function of doping and temperature, interpreted in terms of the semicrystalline nature of the polymer films. In my opinion, the manuscript has some strengths, but also some serious weaknesses. I cannot recommend publication. I think it could be appropriate to consider a majorly revised version in the future, but I admit that I have some reservations that will be hard to address without new data, analyses, interpretation, and discussion. Specific criticisms are raised below.

1. The device in Figure 1 appears to reveal a two terminal measurement. The Methods section also speaks of quasi 4 wire. If these data are all taken two-terminal, then the authors should be explicit about this. This would raise a very serious problem. Quite rightly, many people will simply not believe detailed quantitative and subtle analyses of transport data taken without a four wire approach. The four wire measurement in the ion gel gated system is also standard, and not so difficult to design and do. So can the authors comment on how the measurements were made, why four terminal was not done (if this is so), and why the subtle analyses should be believed if it is two wire data?

2. The introduction and discussion of equations 1-4 generate numerous misconceptions, which spill over into the analyses.

(a) First, the only fully consistent definition of a metal is in terms of finite conductivity in the T goes to zero limit. The T derivative of sigma is decoupled from this, and this causes much confusion in this manuscript. It is not strictly correct to refer to metallic conduction at high T, which becomes localized at low T. The metal is only defined at low T. The “metallic” state at high T is an effectively metallic state, where the localizing factors such as domain boundaries are obscured by thermal effects. This distinction is not made in this work, and it can only cause further confusion in my view.

(b) The authors should be similarly careful with the use of the word “coherent” as on page 3. Precisely, what is meant?

(c) Equation 2 is poorly explained. Following from simple algebra the To value is highly dependent on the exponent. The quoted range is not at all a true range. In 3D Mott VRH, To of 10^6 is easily obtainable. It must also be made clear that the first three exponents cited are for Mott VRH, while the ½ is for ES. In ES, how is the coulomb potential in a solid “unscreened”?

3. The electrochemical doping process wherein anions in the gel infiltrate the film is well established in some polymer systems, but is this so here in PBTTT? What is the evidence? This must at least be addressed here as it impacts the issue of dimensionality, which is important (see below). As an aside, in a semicrystalline system what is known about the homogeneity of the 3D electrochemical gating process? How do the authors know that the dopant ions are homogeneously distributed between domains and walls. This is very important for their analysis.

4. Fig. 1d is hard to understand. The Ig curve shows hysteresis, and the transfer curve appears to also, but one branch seems to be labeled “I” while the other is labeled “sigma”. Please clarify and improve the plot, and discuss the hysteresis (if there is indeed some).

5. Starting in Fig. 1(e), and continuing, the authors take the negative MC at high T as some kind of indicator of metallic transport. I absolutely cannot understand this. Ordinary MR (parabolic, positive) occurs in metals and semiconductors, and scales with mobility. I cannot see how this

provides any evidence of metallic transport.

6. Starting on page 6, my point 2(a) starts to become a real problem. Applying the real definition of a metal, Fig 2a seems to indicate metallicity at -1.7 V to -2.2 V, as the T goes to zero extrapolation is finite. If the authors want to interpret the decreasing sigma in terms of weak localization then dimensionality, barely mentioned in this work, becomes hugely important. In 2D, weak localization is logarithmic and eventually the conductivity falls to zero. In 3D, however, the weak localization is a power law correction to sigma and resistivity does not diverge. Which interpretation are the authors following? Have the data been analyzed for 3D WL?

7. The discussion of figs 2a and 2b is troubling, and incorrect. The gradual variation in a in the Zabrodskii plot is completely normal. The limiting value deep in the insulating phase is 0.5 here, indicating ES VRH, as expected. The decrease at low gate voltage magnitudes need not have anything to do with dimensionality. At constant base T, as the insulator-metal is approached by doping, the onset of VRH at low T will eventually be pushed beneath the minimum measurement T and an ambiguous exponent will be seen. This would happen in a perfectly homogeneous 3D specimen. The smooth crossover from VRH to WL will also lead to a lnT dependence (fig. 2a). A log on a Zabrodskii plot will just show up as a low power. There is no dichotomy between these two figure panels, despite the numerous comments to the contrary.

8. In the deep insulating limit, is there a crossover from slope ½ to ¼ in the -1.3 and -1.4 V data? It looks like it, and this could greatly clarify the situation, indicating that it is indeed 3D conduction!

9. This is major point, relating to points 3, 6, and 7 above. The authors simply state that WL gives ln T. This is true only in 2D! What is the justification for low D transport here? Why do other aspects of the data look 3D? This really must be clarified. Yet worse, in 2D, the ln T dependence is identical for both WL and electron-electron interaction effects. How do the authors, with no consideration or analysis of this point, then know that WL is dominating the T dependence?

10. On line 162 the authors talk of a remarkable deviation from log T below 20 K. I simply do not see it.

11. I believe it is inappropriate to analyze the MC data in terms of mixed VRH and WL effects without mentioning and ruling out the obvious possibility of weak antilocalization.

12. Starting on line 178, we run into another conceptual problem. The authors talk of VRH in Fig 3c, even though there is WL-like MC, like it is a dichotomy. But again, it is not. The VRH only turns on below about 20 K as clearly shown from the Zabrodkii plot. The MR at temps above this can certainly show other effects, and this is normal. At high T, even a film with VRH in the low T limit will show different temperature and field dependence than classic VRH behavior. The Coulomb gap has been smeared by thermal fluctuations, Mott VRH is also gone, and an apparent non-strongly-localized regime will occur.

13. The points above render moot detailed discussion of Fig. 4, which is the central result of this work.

Response to referees

[Reply to the Comments by the Reviewers]

Reviewer #1

We are pleased to know about the reviewer's highly positive evaluation of our work. The followings are the answer to the comment.

(Reviewer's Comment)

The only minor comment is that while this work lays the foundation for understanding better thermoelectricity in organic semiconductors, I doubt that it is suitable for high performance wearable devices as such. The authors should tone down this statement in the abstract and conclusions.

Reply: Conducting polymers, at this stage, may be inferior to other flexible device candidates such as inorganic materials and carbon nanotubes present in thermoelectric device performance, however, we believe that they are promising in the future taking advantage of light-weight, environmental abundance, and facile and low-cost production of large-area devices.

In the revised manuscript, we have modified the last phrase in the abstract and the last sentence before the conclusion.

Reviewer #2

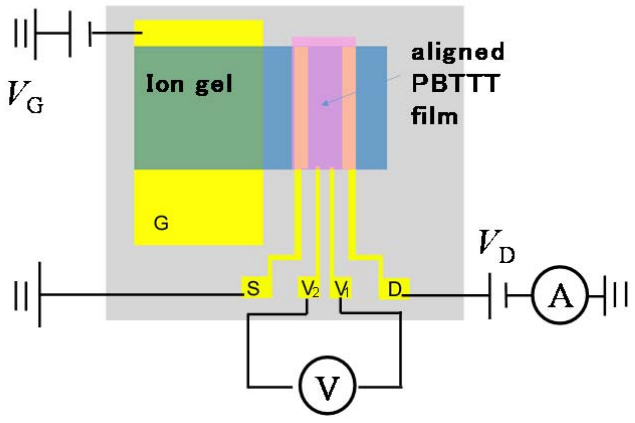
We are much grateful for examining our manuscript in great details and giving us number of valuable comments. We have revised the manuscript and supplementary information taking full account of your opinions and suggestions. We have added new experiments measured by four-terminal technique to evaluate the validity of the data measured with two-terminal method, as shown in Figs. S4 and S5. We also carried out the angle-dependent magnetoconductance measurements under tilted magnetic field to evaluate the applicability of the two-dimensional model, as shown in Figs. S6 and S7. These new experiments were performed with Mr. Katsuya Watanabe, so we invite him as an additional co-author. Based on results of new experiments, the quality of the

experimental evidences is much improved and the analysis and discussions have been much strengthened. In the following we reply for the reviewer's comments one-by-one.

1. The device in Figure 1 appears to reveal a two terminal measurement. The Methods section also speaks of quasi 4 wire. If these data are all taken two-terminal, then the authors should be explicit about this. This would raise a very serious problem. Quite rightly, many people will simply not believe detailed quantitative and subtle analyses of transport data taken without a four wire approach. The four wire measurement in the ion gel gated system is also standard, and not so difficult to design and do. So can the authors comment on how the measurements were made, why four terminal was not done (if this is so), and why the subtle analyses should be believed if it is two wire data?

Reply: We appreciate the reviewer for this important comment. The data presented in the paper were measured by two-terminal method (pseudo four-terminal measurement excluding lead wire resistance). In order to measure the intrinsic electric resistance of a substance, we agree that four-terminal conductivity measurements without the influence of contact resistance are preferred.

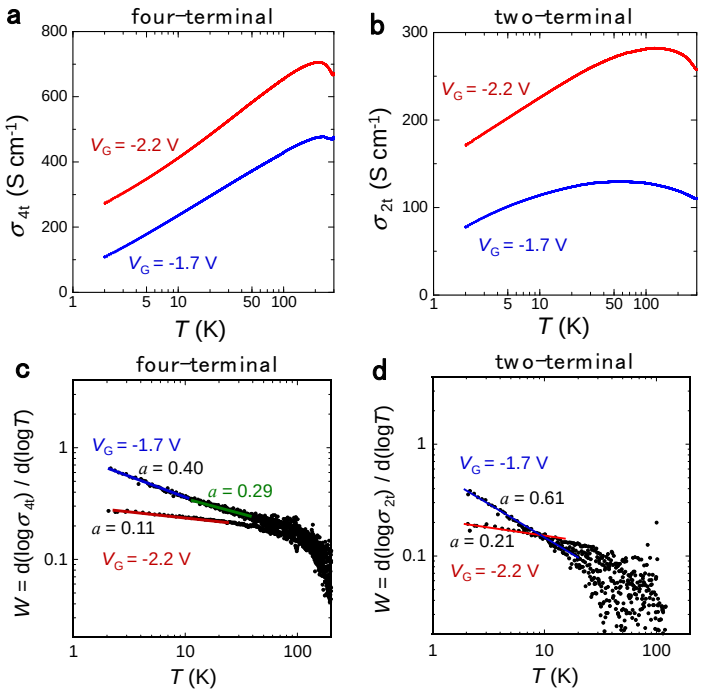
In order to verify the validity of the results measured with two-terminal method, we have performed four-terminal measurements of temperature dependence of conductivity $\sigma(T)$ and magnetoconductivity (MC). We have prepared a device for four-terminal measurements as shown in Fig. S3 in the revised Supplementary Note 3.



Supplementary Figure S3 | Schematic diagram of the device for four-terminal measurements.

We show results at gate voltages $V_G = -2.2$ V and $V_G = -1.7$ V to confirm the difference in behavior of $\sigma(T)$ and MC between four-terminal and two-terminal analyses measured simultaneously. Note that these new data were measured on polymer films with aligned main chain by flow-coat technique. The details of the fabrication for this device are written in the revised Supplementary Note 3.

First, we examine $\sigma(T)$. Fig. S4 in the revised Supplementary Note 3 shows the ln T and Zabrodskii plots of the data obtained by four-terminal and two-terminal analyses of the same experiment. The direction of the change from effectively metallic behavior at high temperatures to VRH at low temperatures was qualitatively the same, and also common to that shown in Fig. 2 measured on spin-coated film with two-terminal method.



Supplementary Figure S4 | ln *T* and Zabrodskii plots of the four-terminal (a and c) and two-terminal (b and d) *σ* measured for the aligned film.

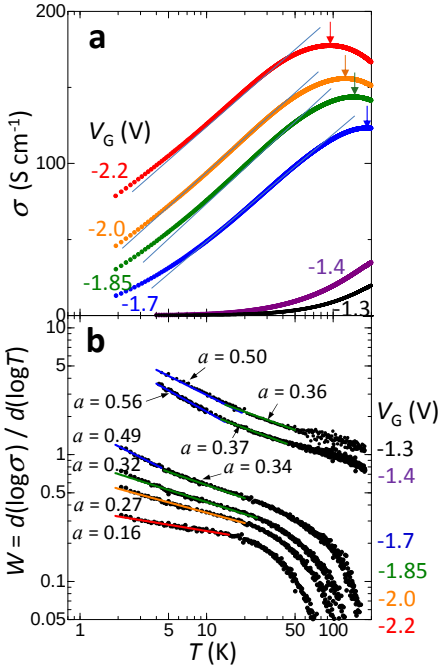
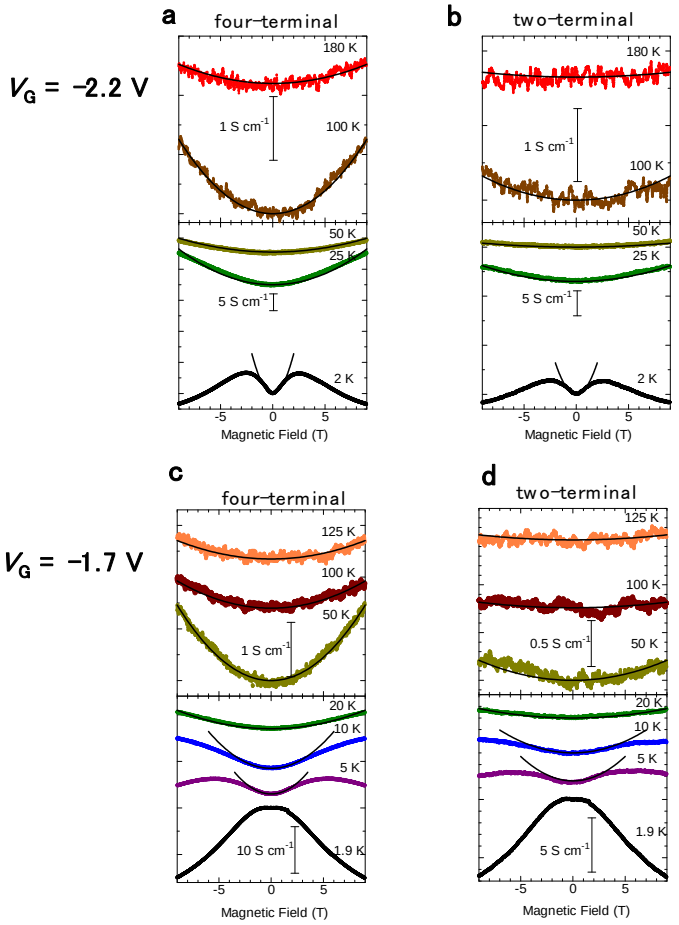


Figure 2 | ln *T* (a) and Zabrodskii (b) plots of the conductivity measured on the spin-coated film with two-terminal method. (main text)

Next, we show in Fig S5 the results of MC at $V_G = -2.2$ V and $V_G = -1.7$ V obtained by four-terminal and two-terminal analyses. The four-terminal and two-terminal results are qualitatively the same and common also to the corresponding two-terminal data in Fig. 3 of the spin-coated film described in the main text, showing positive MC above 20 K and mixture of negative MC component below 10 K. The similarity of the MC behavior between four-terminal and two-terminal measurements could be ascribed to the negligible magnetic field effect on the contact resistances. The negative MC at high temperature side was not observed at 180 K for $V_G = -2.2$ V, which is consistent to the absence of the effectively metallic behavior at this temperature. Quantitatively, however, the magnitude of the absolute value of $\Delta\sigma(B) = \sigma(B) - \sigma(0)$ was ten times (at ~100 K) and several times (at ~10 K) larger in the four-terminal measurements.



Supplementary Figure S5 | Temperature dependence of the magnetoconductivity for the aligned film at V_G = −2.2 and −1.7 V, by four-terminal (a and c) and two-terminal (b and d) analyses of the same measurement, respectively.

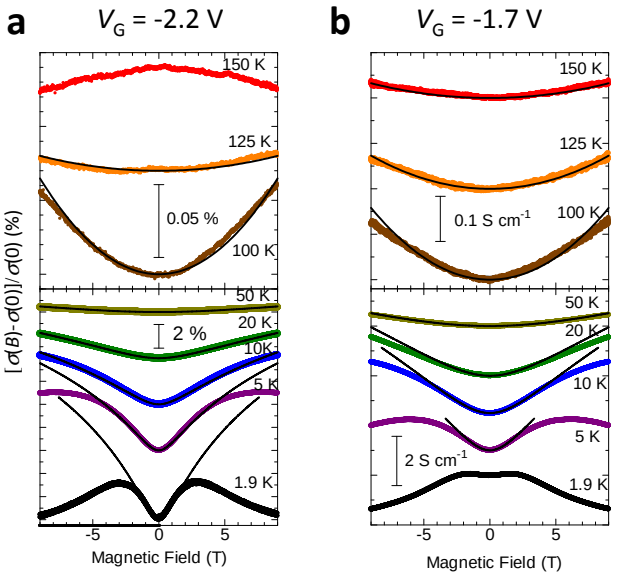


Figure 3a and S2a | Temperature dependence of the magnetoconductivity measured on the spin-coated film with two-terminal method. (Fig. 3a in main text and Fig. S2a in the Supplementary Information.)

Based on these results, we can justify the use of the results using two-terminal measurement to discuss the characteristics of the $\sigma(T)$ and MC indicating changes from effectively metallic to WL and finally to VRH conduction. Moreover, these results demonstrate the universality of the transport behavior of PBTTT films doped with ionic gel, indicating that the results were almost the same even under different film forming conditions.

In the revised manuscript, we write explicitly the fact that the two-terminal method was applied in the experimental data in the main text at the beginning of the Results and discussion section. The additional four-terminal experiments and comparison to the two-terminal data are explained in the main text adding new subsection in Result and Discussion section. The experimental data observed by the four-terminal measurements are included in Figs. S4, S5 in the revised Supplementary Note 3. To compare the absolute value of MCs in two-terminal and four-terminal measurements, the both data are expressed as $\Delta\sigma(B) = \sigma(B) - \sigma(0)$, not the percentage of variation as were in the previous manuscript.

2. The introduction and discussion of equations 1-4 generate numerous misconceptions, which spill over into the analyses.

(a) First, the only fully consistent definition of a metal is in terms of finite conductivity in the T goes to zero limit. The T derivative of sigma is decoupled from this, and this causes much confusion in this manuscript. It is not strictly correct to refer to metallic conduction at high T, which becomes localized at low T. The metal is only defined at low T. The "metallic" state at high T is an effectively metallic state, where the localizing factors such as domain boundaries are obscured by thermal effects. This distinction is not made in this work, and it can only cause further confusion in my view.

Reply: We appreciate the reviewer for this important comment. We agree with the reviewer that the strict definition of the metal should be referred to the ground state that the finite σ remains at $T \rightarrow 0$ limit. The observed $d\sigma/dT<0$ should be expressed as "effectively metallic" state. We add "effectively" at every metallic state we refer in this manuscript.

Because of the inhomogeneity of the polymer films structure consisting of crystalline domain and disordered boundaries, it is difficult to discuss metallicity at low temperatures. We discuss the macroscopic metallicity only when the localizing factors such as domain boundaries are obscured by thermal effects, as in the reviewer's word.

In the revised manuscript, we have written the definition of the "effectively metallic" behavior in the introduction part (Page 4). We use the term "effectively metallic" throughout the text and in short "metallic" in the phase diagram of Fig 4a.

(b) The authors should be similarly careful with the use of the word "coherent" as on page 3. Precisely, what is meant?

Reply: We agree with the reviewer. When the weak localization is occurring, we have expressed it as 'coherent' in the sense that the phase correlation of the carrier wavefunction is preserved, but it is not always completely coherent in phase.

In the revised manuscript, we define this situation as "phase-correlative transport" or simply "delocalized transport".

(c) Equation 2 is poorly explained. Following from simple algebra the To value is highly dependent on the exponent. The quoted range is not at all a true range. In 3D Mott VRH, To of 10^6 is easily obtainable. It must also be made clear that the first three exponents cited are for Mott VRH, while the ? is for ES.

Reply: We appreciate the reviewer's comment. We did not describe the detailed procedure for the fitting to VRH models to obtain parameters in the previous manuscript.

In the revised manuscript, we describe the variable-range hopping model more precisely in the main text (Page 7) and the procedure in the Supplementary Note 1 with Table S1 of the exponent a and T_0 derived from the measured $\sigma(T)$. T_0 is the value fitted when the exponent a is fixed to the value of each VRH model. Since the conductivity is high enough even at the lowest voltage in this study reaching 20 Scm^{-1} at room temperature, T_0 is not so high as 10^6 observed in the case of highly insulating polymers, but we find T_0 of order 10^3 at higher temperature side of Mott's VRH at low gate voltages (See item 8).

In ES, how is the coulomb potential in a solid "unscreened"?
Reply: In the ES-VRH, carriers feel a soft gap on the Fermi surface due to Coulomb interaction, although the Coulomb interactions are not "unscreened".

In the revised manuscript, we rewrite this part as, "In the strongly localized regime where Coulomb interaction is important, Efros and Shklovskii discussed that the exponent is $a = 1/2$ for every dimension (ES-VRH)"

3. The electrochemical doping process wherein anions in the gel infiltrate the film is well established in some polymer systems, but is this so here in PBTTT? What is the evidence?
This must at least be addressed here as it impacts the issue of dimensionality, which is important (see below). As an aside, in a semicrystalline system what is known about the homogeneity of the 3D electrochemical gating process?
How do the authors know that the dopant ions are homogeneously distributed between domains and walls. This is very important for their analysis.

Reply: We appreciate the reviewer for this important comment. As for the structural evidences of the electrochemical doping and two-dimensionality of the PBTTT film, we have measured X-ray diffraction under ion gel gating as shown in Fig. 2 of ref. 13; Tanaka, H. *et al.*, *Sci. Adv.* **6**, eaay8065 (2020).

The lamellar peaks were found in the out-of-plane direction showing 'edge-on structure',
in which the main chain direction with the highest conductivity and the π stack direction with the second highest conductivity are both in the two-dimensional film plane. Therefore, two-dimensional conduction is expected, as is discussion in later items.

The 'edge-on structure' is also confirmed by the angle dependence of the g value of the gate-voltage-induced ESR carrier signal in Fig. S4 of ref.13 and in Fig 4 of ref. 34; Tanaka, H. *et al.*, *Appl. Phys. Lett.* **107**, 243302 (2015).

By applying the gate voltage, the diffraction peak in the lamellar direction shifts to the lower angle side. The lattice constant in the lamellar direction increases, and its size corresponds to the dopant size. It shows that the dopant intercalates into the alkyl chain part of the film. Since the entire diffraction peak is completely shifted, no undoped region remains in the crystalline region confirming that the film is homogeneously doped.

Although no information is obtained for the boundary region by X-ray diffraction, however, ESR signal tells us that the polymers in the boundary region also takes the 'edge-on structure'.

In the revised manuscript, we refer our X ray diffraction measurements in the main text in Page 5 briefly and discuss the two-dimensionality of the film structure at Page 11.

4. Fig. 1d is hard to understand. The Ig curve shows hysteresis, and the transfer curve appears to also, but one branch seems to be labeled "I" while the other is labeled "sigma". Please clarify and improve the plot, and discuss the hysteresis (if there is indeed some).

Reply: We are sorry that the confusion arose because the I_D and σ symbols appeared to point only one side of the hysteresis curve. The drain current I_D corresponds to the left

axis and the same data corresponds to the right σ axis in both the increasing and decreasing directions of the gate voltage sweep. In the revised manuscript, the arrows to point the right and left axes in Fig. 1d are changed to start with circles surrounding both curves measured during the going and returning voltage sweep.

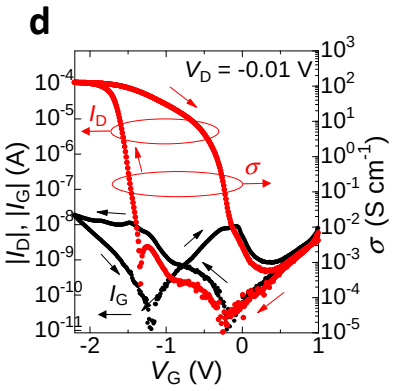


Figure 1d. | (d) Transfer characteristics and gate current of the device operated at room temperature.

5. Starting in Fig. 1(e), and continuing, the authors take the negative MC at high T as some kind of indicator of metallic transport. I absolutely cannot understand this. Ordinary MR (parabolic, positive) occurs in metals and semiconductors, and scales with mobility. I cannot see how this provides any evidence of metallic transport.

Reply: We appreciate the reviewer for the comment. We agree that the negative parabolic MC is observed in both metals and semiconductors exhibiting band-like transport. Thus, we cannot take the negative MC itself as an indicator of the metallic transport.

However, in the present case, since the negative MC is observed on the high temperature side of the WL, it is unlikely to be that of a semiconductor in which the activation-type conductivity is expected, and it is natural to be interpreted that 'effective metallic behavior' is observed without the influence of WL. Moreover, by the electron spin resonance study, a metallic signature (Pauli magnetic susceptibility) is observed within the crystalline domain as in Fig. 3 of ref. 13 and in Fig 5 of ref. 34, and it is

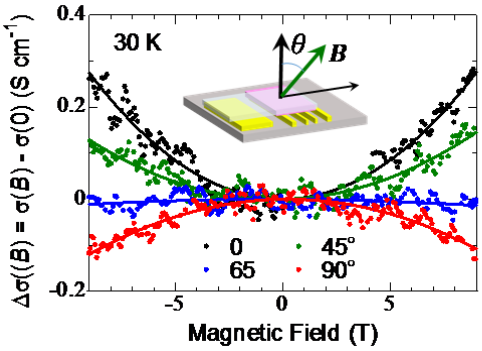
sufficiently expected that macroscopic metal-like conduction will appear when the influence of the boundary barrier disappears at high temperature.

In the revised manuscript, we write that "The negative MC is consistent with the effectively metallic transport" in the first subsection of Results and discussion section and add discussions on the effective metallic state at later subsections (Page 12).

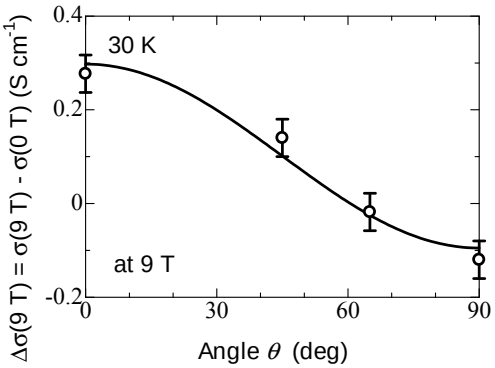
6. Starting on page 6, my point 2(a) starts to become a real problem. Applying the real definition of a metal, Fig 2a seems to indicate metallicity at -1.7 V to -2.2 V, as the T goes to zero extrapolation is finite. If the authors want to interpret the decreasing sigma in terms of weak localization then dimensionality, barely mentioned in this work, becomes hugely important. In 2D, weak localization is logarithmic and eventually the conductivity falls to zero. In 3D, however, the weak localization is a power law correction to sigma and resistivity does not diverge. Which interpretation are the authors following? Have the data been analyzed for 3D WL?

Reply: We agree that the dimensionality of the transport is quite important. In 3D-WL, positive MC$\propto H^2$ is observed at low magnetic field, and positive MC$\propto H^{1/2}$ at high magnetic field. Since this dependence does not change much in 2D, distinguishing the 2D and 3D WL is in principle difficult even by using the MC measurement at a fixed magnetic field direction. Then, we have newly measured the angle dependence of MC described in Supplementary Note 4.

We show in Fig. S6 the result of angle-dependent MC measurements at 30 K at the gate voltage of $V_G = -1.7$ V, where positive MC is observed under magnetic field applied perpendicular to the film. As a result, two-dimensional anisotropic behavior was observed scaled with $\cos^2\theta$ as shown in Fig. S7. This is qualitatively the same as reported for F4TCNQ-doped PBTTT in ref. 8, Kang, K. *et al.*, *Nat. Mater.* **15**, 896-902 (2016). The anisotropy also agrees with that reported by Zanettini S. *et al.*, *Appl. Phys. Lett.* **106**, 063303 (2015) (ref. 24 of the revised manuscript) at low temperature.



Supplementary Figure S6 | Angular dependence of magnetoconductivity at 30 K, V_G = −1.7 V measured by four-terminal method. The solid lines are asymptotic parabolic curves.



Supplementary Figure S7 | Angular dependence of magnetoconductance at 30 K, V_G = −1.7 V at 9 T as a function of the angle θ between the normal of the film and magnetic field. The solid curve represents a fit to $\cos^2\theta$.

Based on our angle-dependent MC and those reported by Kang and Zanettini *et al*., we can consider that the electrical conduction of PBTTT film is 2D in which weak localization is logarithmic, although the criterion whether the conductivity falls to zero at absolute zero is hard to be applied because of the effect of domain boundary at low temperature.

The 2D conduction in the present PBTTT film is expected for thin film samples taking 'edge-on structure' in which most and second most conducting directions lay within the film plane, as shown in ref 13 and references therein. This is in strong contrast to the

cases of conduction polymers studied in 1980-1990s with rather thick bulk films which are well treated with 3D models.

In the revised manuscript, we add a section for the angular dependence of MC to confirm the validity of the use of 2D model for the present polymer film.

7. The discussion of figs 2a and 2b is troubling, and incorrect. The gradual variation in a in the Zabrodskii plot is completely normal. The limiting value deep in the insulating phase is 0.5 here, indicating ES VRH, as expected. The decrease at low gate voltage magnitudes need not have anything to do with dimensionality. At constant base T, as the insulator-metal is approached by doping, the onset of VRH at low T will eventually be pushed beneath the minimum measurement T and an ambiguous exponent will be seen. This would happen in a perfectly homogeneous 3D specimen. The smooth crossover from VRH to WL will also lead to a lnT dependence (fig. 2a). A log on a Zabrodskii plot will just show up as a low power. There is no dichotomy between these two figure panels, despite the numerous comments to the contrary.

Reply: We appreciate your comment that the VRH exponent seems to be normal. We believe that our basic understandings are not so far from the reviewer's ones, however, this was not written explicitly in the previous manuscript. We think it is natural to observe a gradual variation of the exponent a in the Zabrodskii plot with respect to T and doping level in such inhomogeneous polymer films. As the reviewer pointed out, at the lowest gate voltage, $a = 0.5$ is almost accurate at least in the low temperature region where positive MC according to WL is absent. We think it should be understood by normal ES-VRH. At $V_G = -1.4$ V, -1.7 V, and moreover at $V_G = -1.3$ V (See item 8) there is a change in exponent that can be interpreted as a crossover from ES to Mott. Again, this is the same behavior reported so far.

Our understandings, based on the MC measurements, are that the variation of the exponent a is affected if the contribution of WL appears. At $V_G = -1.7$ V, the contribution of WL appearing in MC extends to the low temperature where the coefficient is determined by the Zabrodskii plot, and in that temperature region, the effect of WL also appears in σ(T), and as the reviewer pointed out "*smooth crossover from VRH to WL* " occurs.

The use of Fig. 2a, in addition to the Zabrodskii plot in Fig. 2b is to stress the effect of

2D WL showing ln *T* dependence, which is also observed in our four-terminal results of the aligned films. We agree with the reviewer that that there is no dichotomy between these two figures; the Zabrodskii plot is also important for clarifying the VRH behavior at low temperatures, indicating that both panels are equally important. Then, we use both figures in the manuscript.

In the revised manuscript, we have fully rewritten the discussion on the Zabrodskii analysis with a table of obtained parameters in the Supplementary Note 1 and mention explicitly the crossover from ES to Mott-VRH as a function of temperature.

8. In the deep insulating limit, is there a crossover from slope ? to ? in the -1.3 and -1.4 V data? It looks like it, and this could greatly clarify the situation, indicating that it is indeed 3D conduction!

Reply: Thank the reviewer for pointing out that there also exists a crossover even for the $V_G = -1.3$ V data. There is a change in the VRH exponent from 0.50 to 0.36 at $V_G = -1.3$ V and from 0.50 to 0.37 at $V_G = -1.4$ V. It is possible to interpret these as crossovers from ES to Mott 2D-VRH. However, in the temperature range where the slope changes, positive MC already appears and the contribution of WL would exist, so there would be *smooth crossover from VRH to WL* as the reviewer wrote in the item 7.

In the revised manuscript, we add a crossover from ES to Mott VRH also at $V_G = -1.3$ V.
The description on the coexistence of VRH and WL is revised in Page 15 and 20.

9. This is major point, relating to points 3, 6, and 7 above. The authors simply state that WL gives ln T. This is true only in 2D! What is the justification for low D transport here? Why do other aspects of the data look 3D? This really must be clarified. Yet worse, in 2D, the ln T dependence is identical for both WL and electron-electron interaction effects. How do the authors, with no consideration or analysis of this point, then know that WL is dominating the T dependence?

Reply: We thank the reviewer for pointing out the contribution of electron-electron interaction (EEI) effect, which has not been taken into account in the previous manuscript. In the Anderson localization, weak localization occurs in conjunction with the electron-electron interaction effect which give rise to negative MC. We cannot rule

out the contribution of the EEI effect relevant to the WL effect, as found by the angle rotation experiments shown below.

By the analysis of the angle-dependent MC measurement, we find an isotropic negative MC, which is ascribed to EEI, as is also discussed in Ref. 8.

Note that the negative MC component originated from the EEI effect is opposite direction to 2D-WL. Because of such component, the magnitude of the positive MC due to WL may be larger below ~30 K. As a result, the calculated λ may be longer within a factor of 2, but λ is still within the size of crystal domain.

Since WL is considered to be generated from such a crystalline region, it is consistent with the fact that the positive MC component has a two-dimensional result from the angle dependence experiment of the magnetoresistance. As described in item 3, in the X-ray structural analysis, lamella peaks are observed only in the out-of-plain direction, and the main chain direction with the highest conductivity and the π stack direction with the second highest conductivity are both in the two-dimensional plain. It has been confirmed that a certain edge-on structure is adopted, and it is sufficiently reasonable that the crystal region observed by X-ray exhibits two-dimensional conduction.

Regarding the temperature dependence of ln$T$, as the reviewer pointed out, the temperature dependence of ln$T$ in a two-dimensional system also appears due to electron-electron interaction (Ref. 11, Sec III F). However, the EEI effect also appears under Anderson localization, and it is not necessary to distinguish it from that caused by WL.

In the revised manuscript, we write the effect of EEI to give rise to the negative MC upon the analysis of MC. At low temperatures, because EEI effect is relevant to the WL which gives rise to significant negative MC, it is difficult to separate VRH contribution from WL when both component is visible. In the revised manuscript, we deleted the Supplementary Note section describing the separation of WL and VRH and delete λ data points obtained by separating the negative MC component from Fig. S8.

10. On line 162 the authors talk of a remarkable deviation from log T below 20 K. I simply do not see it.

Reply: We appreciate you comment. According to the suggestion, straight auxiliary lines are drawn with the semi-logarithmic plot of Fig 2a so that the deviation from ln$T$ at low temperature side can be recognized.

11. *I believe it is inappropriate to analyze the MC data in terms of mixed VRH and WL effects without mentioning and ruling out the obvious possibility of weak antilocalization.*

Reply: We thank the reviewer for pointing out the possibility of the antilocalization effect. Negative MC also appears due to the weak antilocalization effect when the spin-orbit coupling is strong. The occurrence of antilocalization effect is often limited to the low magnetic field range less than 1 T, however, out observation of the negative component is rather at high field region. Moreover, the conductive polymer and ion gel used in this study are all composed of elements with atomic numbers smaller than sulfur, and the spin-orbit interaction is considered to be small.

In the revised manuscript, we add the short discussion on the weak antilocalization in the main text, where Hikami-Larkin-Nagaoka model is applied to analyze the MC (Page 13).

12. Starting on line 178, we run into another conceptual problem. The authors talk of VRH in Fig 3c, even though there is WL-like MC, like it is a dichotomy. But again, it is not. The VRH only turns on below about 20 K as clearly shown from the Zabrodkii plot. The MR at temps above this can certainly show other effects, and this is normal.
At high T, even a film with VRH in the low T limit will show different temperature and field dependence than classic VRH behavior. The Coulomb gap has been smeared by thermal fluctuations, Mott VRH is also gone, and an apparent non-strongly-localized regime will occur.

Reply: We appreciate your comment on the relation between WL and VRH. In Fig. 3c, we observe WL-like positive MC above 20 K, and negative MC below 20 K. It is reasonable to interpret this negative MC in terms of VRH, because the Zabrodskii plots below 20 K are likely to have VRH contributions and analyzed as shown in the Supplementary Note 5. However, we are aware of the contribution from EEI for negative MC, in the temperature range where the WL is observed, so that the dichotomic analysis indicated in the previous Supplementary Note is hard to be applied.

Thus we have deleted the section from the Supplementary Information.

When a positive MC appears, it is unlikely to be considered for anything other than weak localization except for organic magnetoresistance (OMAR) in the low magnetic field mT region of the sandwich structure. Because the positive MC has a magnetic field dependence close to that of a parabola, we think that the "apparent non-strongly-localized regime" can be ascribed to the weak localization.

As for the critical temperature where the positive MC turns on, the coloring in Fig. 4a in the previous manuscript was not correctly separated for the boundary between WL+VRH and pure VRH, whether positive MC is observed. In the revised manuscript, the coloring is modified to represent the experiment more precisely.

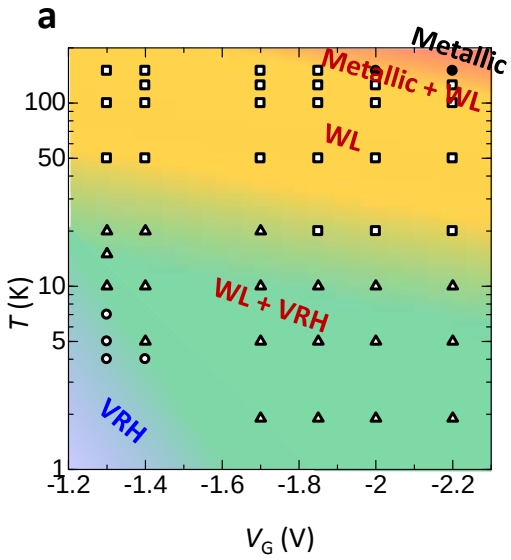


Figure 4a | T–V_G schematic diagram of the conduction mechanism consisting of Metallic, Metallic+WL, WL, WL+VRH, and VRH regions, based on the MC measurements.

13. The points above render moot detailed discussion of Fig. 4, which is the central result of this work.

Reply: Thanks to your comments above, we are now aware of problems in the previous manuscript. First one is the four-terminal measurement. Because we got qualitatively the same result with those of two-terminal measurement, we can justify the use of the

results using two-terminal measurement to capture the characteristics of $\sigma(B)$ from effectively metallic to VRH conduction via WL.

The second one is the applicability of 2D model for the analysis, which was verified by the angle-dependent MC measurements.

The third one is the EEI effect for the negative MC. In the WL region, the presence of negative MC component should be taken into account. Then, the positive MC is 1.5 times as large as previous calculation at 30 K, that changes the value of λ within twice. This does not change the conclusion that the nucleation of WL occurs within the crystallite

Therefore, the phase diagram in Fig. 4a almost stays valid and the discussions based on this remain almost unchanged, except that the boundary between metallic behavior and WL on the high temperature side shifts and that the boundary between WL+VRH and VRH was incorrect, as noted in item 12.

REVIEWERS' COMMENTS:

Reviewer #2 (Remarks to the Author):

The authors provided a detailed rebuttal to my criticisms in the first round of reviewing. I accept most points/responses/revisions, but there remain a handful of problematic ones, which I discuss below, using my original numbering.

1. I am pleased that the authors now make clear in the manuscript that the data were indeed all taken on 2 terminal devices. I fear many readers would not have detected this. The authors have now taken proper data at two gate voltages and are using it to support the claim that two terminal data are OK. I think many people will be convinced by this. I have to add, however, that (a) I am not convinced, personally, and (b) there will be a fraction of the community that simply drop this manuscript when they read that it is not four terminal. My own opinion is based on the fact that the "verifications" of similar results in two and four terminal cases is not convincing. First, they were performed at fairly high voltage magnitudes, where contact effects will be weaker than on the insulating samples. Second, the exponents in the relevant Zabrodskii figure clearly move around quite a bit. Third, there are cases shown here where the two terminal resistance (which includes the contacts) is less resistive (more conductive) than the four terminal. This is hard to understand unless the sample-to-sample variations are so big that the comparison is inappropriate. For these reasons, I am not convinced, although I reiterate that I think most casual readers will be.

2c. The authors seem to have missed my point. I was not saying that the range I am stating is what they see. I was simply saying that the To value of course changes massively with the exponent, due to simple arithmetic. In any case, it does not matter so much in the revised version of the manuscript.

5. I cannot concede this point. The authors now state that the positive MR at high T is "consistent" with the effectively metallic behavior. My point is that it is also consistent with the exact opposite, i.e., semiconducting behavior. I continue to think this is highly misleading.

With respect to the revised version, the manuscript is indeed now considerably improved, as many of the inaccuracies and ambiguities have been addressed. There is no doubt that it is better, and, based on the other referee report, might be headed towards acceptance. I continue to feel that there are serious flaws, but I certainly agree that it is substantially improved.

Reviewer #3 (Remarks to the Author):

The work reported in this manuscript by the group of Taishi Takenobu quantifies the nature of charge transport within an electrolyte-gated organic polymer transistor, and is a significant extension to their earlier work published in Science Advances not very long ago.

The authors show high-quality measurements of the temperature dependent conductivity and the temperature dependent magneto-conductance to chart a gradual transition from a transport regime that shows a metallic behaviour to a regime dominated by variable range hopping (VRH). They clearly rationalise the signatures of weak localisation (WL) in their magneto-conductance, and show that potential intermediate regimes exist on the "conductivity phase diagram" where WL is inter-twinned with either the metallic regime or with the VRH regime.

One of the strongest points of this paper is in giving a deeper meaning to an earlier hand-waving empirical model by Kang and Snyder of the Seebeck coefficient and its dependence on the conductivity. The authors clearly demonstrate here how the physical underpinnings of inter-grain and intra-grain transport can influence the exponent extracted in Snyder's empirical relation.

All in all, this work is a fantastic piece of work that is timely and of very high relevance to the organic electronics community.

The manuscript seems to have already gone through a round of reviews, and the issues raised by the earlier reviewers have been clearly incorporated.

I am very pleased with the current version of the manuscript, and happily recommend it for publication in Communications Physics in its current form.

As an after thought, I'd like the authors to think about a potential experiment for the future. The temperature dependence of the Seebeck coefficient has not been discussed in their current paper, but it is known that chemically doped polymers as well as electrolyte gated polymers show a Seebeck coefficient that trends with the Mott formula. In other words, the Seebeck of a doped polymer shows a metallic character (Seebeck increases with increasing temperature), while the conductivity of the same doped polymer shows an activated hopping-like behaviour (conductivity increases with increasing temperature). I can already see how such observations can be validated based on the author's current analysis, but I would request the authors to attempt demonstrating how their current understanding of grain boundary-impacted charge transport plays a role in the temperature-dependent Seebeck effect at different charge-carrier densities.

If the authors are able to construct a higher dimensional plot of the Seebeck coefficient as a function of the conductivity and temperature, the authors would have found the holy grail that brings charge transport together with thermo-electrics in organic semiconductors. Such a collective understanding would arguably be one of the most impactful contributions to the field of organic electronics in decades.

Response to referees

[Reply to the Comments by the Reviewers]

Reviewer #2

We are pleased to know that the reviewer accepts most points/responses/revisions, although some debatable problems remain. We wish to reply the remaining problem in the following.

1. I am pleased that the authors now make clear in the manuscript that the data were indeed all taken on 2 terminal devices. I fear many readers would not have detected this. The authors have now taken proper data at two gate voltages and are using it to support the claim that two terminal data are OK. I think many people will be convinced by this. I have to add, however, that (a) I am not convinced, personally, and (b) there will be a fraction of the community that simply drop this manuscript when they read that it is not four terminal.

Reply: We are grateful that we could eliminate the possibility of being mistaken for four-terminal measurement and correctly convey the experimental conditions to the reader. We would also like to thank you for giving us the opportunity to add four-terminal measurement data and improve the reliability of the experiment. As the reviewer points out, it would be important to measure all the conductivity with four-terminal technique. We would like to do it in the future.

My own opinion is based on the fact that the "verifications" of similar results in two and four terminal cases is not convincing.

First, they were performed at fairly high voltage magnitudes, where contact effects will be weaker than on the insulating samples.

Reply: Thank you for pointing out. We have performed the four-terminal measurements to validate our two-terminal results only at relatively high gate voltages. As the reviewer says, we strongly feel that four-terminals should be used under all conditions, but in the experiments that we can start immediately, only the high-doped state can be achieved at present. This is partly because we use one-order of magnitude wider channel length for

the four-terminal measurement compared to the two-terminal one, the drain current at low temperature becomes too small to be measured correctly when the doping level is low. Thank you for pointing out. We would like to do the four-terminal measurements in the full doping ranges in the future.

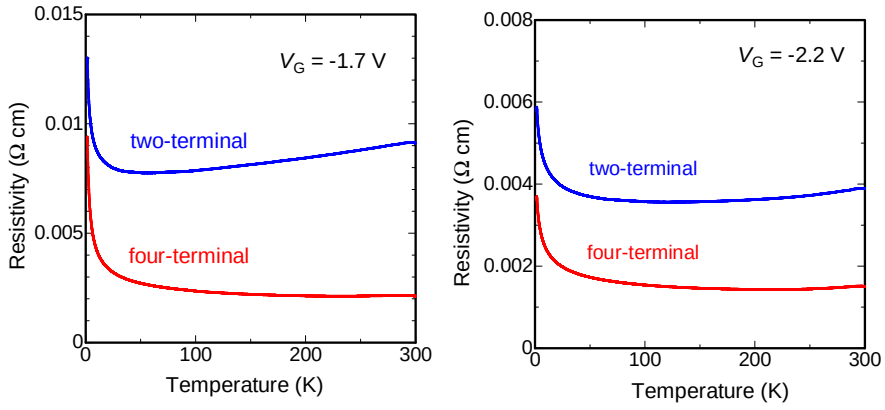
Related explanation is added in the Supplementary Note 3.

Second, the exponents in the relevant Zabrodskii figure clearly move around quite a bit.

Reply: We agree that the exponents in the Zabrodskii analysis change between two-terminal and four-terminal analyses. Nevertheless, we can say that the tendency of the decrease in the exponent from ES-VRH (a = 0.5) to 3D-VRH (a = 0.25) or even lower is common to the two results.

Third, there are cases shown here where the two terminal resistance (which includes the contacts) is less resistive (more conductive) than the four terminal. This is hard to understand unless the sample-to-sample variations are so big that the comparison is inappropriate.

Reply: For the sample we made the simultaneous two- and four-terminal analyses, the two-terminal resistance value is always larger than the four-terminal one in all the measured temperature range, as shown in the figure for V_G = -1.7 and -2.2 V below.



However, the temperature dependence of the two-terminal resistance is metal-like while the four-terminal one is non-metallic in some temperature range around ~ 200 K. We think that this could be because of the temperature dependence of the contact resistance,

whose nature is unknown at present. Detailed study on the temperature dependence of the contact resistance would be a future work.

2c. The authors seem to have missed my point. I was not saying that the range I am stating is what they see. I was simply saying that the To value of course changes massively with the exponent, due to simple arithmetic. In any case, it does not matter so much in the revised version of the manuscript.

Reply: We appreciate the reviewer's comment. We understand that the T_0 value moves around with respect to the exponent value adopted for the fitting. T_0 is obtained by fitting the data to Equation (2) with the exponent *a* fixed to the value of each VRH model. The fitting process is now written explicitly in the Supplementary Note 1 with Supplementary Table 1 in which the full set of the parameters derived from the Zabrodskii analyses are indicated.

5. I cannot concede this point. The authors now state that the positive MR at high T is "consistent" with the effectively metallic behavior. My point is that it is also consistent with the exact opposite, i.e., semiconducting behavior. I continue to think this is highly misleading.

Reply: We appreciate the reviewer for the comment. We agree that the observation of the negative parabolic magnetoconductance itself cannot be the unequivocal signature of the metallic transport. We do not deny other possibility that it can also be consistent with semiconducting behavior.

The negative MC is observed on the high temperature side of the WL where we do not observe the activation-type conductivity characteristic of a semiconductor but observe metallic temperature dependence of the conductivity. Thus, we think that it is natural to interpreted that the negative MC could be of characteristic of the 'effective metallic behavior' without the influence of WL.

In the revised manuscript, we write that "The observation of the negative parabolic MC, i.e., positive magnetoresistance, could be either interpreted as that of a metal or a semiconductor. Since we observe a metal-like temperature dependence, not activation-type temperature dependence, of conductivity at this temperature, it is natural to consider that the negative MC is characteristic of the effectively metallic transport" in

the first subsection of Results and discussion section and add discussions that the interpretation that the negative MC at 150 K is a sign of the effectively metallic conduction could be rationalized since we observe WL behavior at lower temperature side at later subsections (in the middle of Page 12).

Reviewer #3

We are pleased to know about the reviewer's highly positive evaluation on the current version of the manuscript and encouragements for our work on the thermoelectricity. The followings are the answer to the comment.

(Reviewer's Comment)

As an after thought, I'd like the authors to think about a potential experiment for the future. The temperature dependence of the Seebeck coefficient has not been discussed in their current paper, but it is known that chemically doped polymers as well as electrolyte gated polymers show a Seebeck coefficient that trends with the Mott formula. In other words, the Seebeck of a doped polymer shows a metallic character (Seebeck increases with increasing temperature), while the conductivity of the same doped polymer shows an activated hopping-like behaviour (conductivity increases with increasing temperature). I can already see how such observations can be validated based on the author's current analysis, but I would request the authors to attempt demonstrating how their current understanding of grain boundary-impacted charge transport plays a role in the temperature-dependent Seebeck effect at different charge-carrier densities.

Reply: We completely agree with the reviewer that the temperature-dependent Seebeck coefficient measurement is highly important. We should know how the temperature dependence of the conductivity and Seebeck coefficient are understood within the framework of the present study, that is, how the Seebeck effect is understood in each regimes taking account of the role of crystalline domains and domain boundaries. Such study is now underway.