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24th Nov 20

Dear Professor Watanabe,

Thank you for submitting your manuscript, "Supramolecular cocrystals built through redox-triggered ion intercalation in π -conjugated polymers", to Communications Materials. It has now been seen by 3 referees, whose comments are appended below. You will see that they find your work of interest, and raise some points that should be responded to, including some additions to the text. We are interested in publishing your study in Communications Materials, but would like to consider your response to these concerns in the form of a revised manuscript before we make a decision on publication.

We therefore invite you to revise and resubmit your manuscript, taking into account the points raised.

We are committed to providing a fair and constructive peer-review process. Please don't hesitate to contact us if you wish to discuss the revision in more detail.

When submitting your revised manuscript, please include the following:

- A response letter with a point-by-point reply to each of the referee comments and a description of changes made. Please include the complete referee report in the response letter. Please note that the response letter must be separate to the cover letter to the editors.

- A marked-up version of the manuscript with all changes to the text in a different colored font. Please do not include tracked changes or comments. Please select the file type 'Revised Manuscript - Marked Up' when uploading the manuscript file to our online system.

- A clean version of the manuscript. Please select the file type 'Article File'.

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We hope to receive your revised paper within three months; please let us know if you aren't able to submit it within this time so that we can discuss how best to proceed. If we don't hear from you, and the revision process takes significantly longer, we will close your file. In this event, we will still be happy to reconsider your paper at a later date, as long as nothing similar has been accepted for publication at Communications Materials or published elsewhere in the meantime.

We understand that due to the current global situation, the time required for revision may be longer than usual. We would appreciate it if you could keep us informed about an estimated timescale for resubmission, to facilitate our planning. Of course, if you are unable to estimate, we are happy to accommodate necessary extensions nevertheless.

Please do not hesitate to contact me if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

The authors carry out a detailed analysis on PBTTT comparing traditional chemical doping alongside anion exchange doping which they pioneered in a previous publication.

They argue that chemical doping of conjugated polymers can be understood through the process of ion intercalation, where a guest ion intercalates in-between sheets of a 2 dimensional host material which causes the host material to swell to accommodate the new structure, a process similarly described for batteries and ionic conductors.

Using (1) XRD w/electron density modeling, (2) Hall carrier density, and (3) elemental ratios derived from XPS, the authors demonstrate a similar ratio of ~1:1 between the dopant anions / free carriers and polymer monomer units. These complementary techniques form the backbone of their thesis, which is that chemical doping can be considered as the formation of a supramolecular co-crystal between host and guest charged species. Generally doping levels are limited by the redox potential of the guest dopant, however in cases where a sufficiently strong oxidizing agent is used (as in the case with TPA-TFSI here), the ultra-high doping levels observed are indeed limited by the number of dopant anions that may be intercalated inside a given side chain monomer unit for the polymer.

This work has important implications for the polymer doping community where the doping process can be considered as an intercalation problem where carrier densities may be fundamentally related to the composition and charge ratio of the newly formed supramolecular co-crystal. I believe the results are important and worthy of publication in Communications Materials.

I have only a few minor comments. First, the idea that the process of inserting dopants into the polymer lamellae is redox-driven was also recently explored by Aubry et al., *Adv. Funct. Mater.* 2001800 (2020); this work should be cited and compared to the authors' conclusions. In addition, the whole idea that dopants prefer the lamellar regions of conjugated polymer films was first discussed using aligned samples by Hamidi-Sakr et al., *Adv. Funct. Mater.* 1700172 (2017), and this work should also be referenced.

Next, in Fig. 1, the authors compare the conductivity (panel e) and the UPS data (panel f). Given that the conductivity of the Mo-based dopant is so much lower than that after ion exchange, why does the UPS show a similar depletion of the valence band (orange and green)? This implies that the carrier concentration in the two cases are similar, so that the carrier mobilities must be vastly different. Can the authors comment on why this is the case? Similarly, with the red curve, the deeper valence band suggests an even higher doping concentration, but the conductivity is similar to the anion-exchanged film. Does this mean that the carrier mobility is actually lower for this case? Please discuss! Finally, can the authors estimate the density of states in the valence band and use the depletion to actually estimate the carrier concentration and thus carrier mobility in each case? This would be very helpful to the reader!

Finally, a typo at bottom of page 3: "radial salts" needs to be changed to "radical salts"

Reviewer #2 (Remarks to the Author):

This project considers a doping system for conjugated hole-carrying polymers in which an organic donor triarylamine is preoxidized before being inserted into and interacting with the polymer. This system is hypothesized to allow dopants to fit among the polymer chains within a superstructure and lead to high doping efficiency and conductivity. The use of the triarylamine radical cation as a dopant, which ultimately is dissolved and removed as a neutral product, appears novel. The amine thus acts as a cationic component of a salt dopant, with the counterion remaining. The effectiveness of the triarylamine cation depends on its role in inducing or preserving the polymer morphology that is left behind after the neutral amine is removed.

The polymer studied is a well-known high-mobility p-type polymer. The counterion, TFSI, is also well known for its solubility and compatibility with organic materials.

Higher conductivity, good hole mobility, and corresponding higher work function are observed when the new system is used instead of two established p-dopants. An x-ray-determined morphology with counterions in positions that do not interfere with the pi stacks seems to be helpful. Self-consistency among the various characterizations is excellent. The effects are robust with respect to increasing film thickness. An analogy is made to intercalation compounds, in which dopants exist between planes that are fairly undisturbed by the doping.

The structure obtained here is considered ideal for stable, conductive polymers. Indeed, the counterion seems to be superior for stability as well as magnitude of conductivity.

A remaining question seems to be the role of the radical cation in determining the ultimate morphology. Would other triarylamines, or other organic acceptors with different structures, be effective? This issue limits the generality of the structure-activity guidance provided by this paper.

There is a large literature of conducting polymers with conductivities between 100 and 1000 S/cm. This literature and representative values (5-10 additional references, or a couple of reviews that aggregate these data) should be summarized so that the quantitative conductivity enhancements can be evaluated relative to the state of the art.

Otherwise, this is an excellent contribution to the science of conductive polymers.

Reviewer #3 (Remarks to the Author):

In this manuscript, the authors report a novel method to dope conjugated polymers using a triarylamine radical cation. The manuscript also reports the impact of various counterions on the morphology and electrical properties of the conjugated polymer PBTTT. Very recently, Segalman, Chabiny, and co-workers published a paper titled "Effects of Counter-Ion Size on Delocalization of Carriers and Stability of Doped Semiconducting Polymers" in *Adv. Electron. Mater.* (*Adv. Electron. Mater.* 2020, 2000595). This work also looks at PBTTT and the role of counterions. The authors of this work used the ion exchange method developed by Watanabe and co-workers (*Nature*, 2019). Many of the results in the *Adv. Electron. Mater.* Paper are similar to the results presented in this manuscript. The authors may be disappointed to learn about this possible scoop. However, I think that the method to dope conjugated polymers using triarylamine radical cations are still novel. So, I suggest that the authors compare their data and discuss their results in the context of the *Adv. Electron. Mater.*

Minor Suggestions

1. In the literature, the compound triphenylamine is abbreviated as TPA. Here they are using tris(4-bromophenyl)amine. Perhaps they can use an alternate abbreviation to avoid confusion.
2. The authors use a free-energy argument for electron transfer, which is OK from a thermodynamic point-of-view. How does the rate of electron transfer change with dopants or anion? The authors need not answer this question but perhaps comment on the reorganization energies for the dopants, which will impact the kinetics. Is F4TCNQ ineffective because of slow electron transfer or because the thermodynamics favor a partial electron transfer?

[Reply to the Comments by the Reviewers] (Manuscript number: COMMSMAT-20-0339)

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Reviewer #1

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We are grateful for the positive evaluation particularly of our experimental results. We have carefully considered his/her suggestions, and revised the manuscript accordingly.

(Reviewer's Comment 1)

I have only a few minor comments. First, the idea that the process of inserting dopants into the polymer lamellae is redox-driven was also recently explored by Aubry et al., Adv. Funct. Mater. 2001800 (2020); this work should be cited and compared to the authors' conclusions. In addition, the whole idea that dopants prefer the lamellar regions of conjugated polymer films was first discussed using aligned samples by Hamidi-Sakr et al., Adv. Funct. Mater. 1700172 (2017), and this work should also be referenced.

(Our Reply 1)

We appreciate the reviewer for listing related works. According to the reviewer's suggestions, we added two references in the revised manuscript.

(Reviewer's Comment 2)

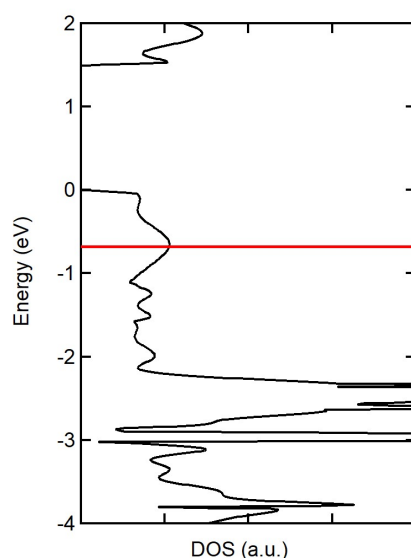
Next, in Fig. 1, the authors compare the conductivity (panel e) and the UPS data (panel f). Given that the conductivity of the Mo-based dopant is so much lower than that after ion exchange, why does the UPS show a similar depletion of the valence band (orange and green)? This implies that the carrier concentration in the two cases are similar, so that the carrier mobilities must be vastly different. Can the authors comment on why this is the case? Similarly, with the red curve, the deeper valence band suggests an even higher doping concentration, but the conductivity is similar to the anion-exchanged film. Does this mean that the carrier mobility is actually lower for this case? Please discuss! Finally, can the authors estimate the density of states in the valence band and use the depletion to actually estimate the carrier concentration and thus carrier mobility in each case? This would be very helpful to the reader!

(Our Reply 2)

The reviewer's comment are spot-on. We should have clarified these more. The reviewer is correct that the carrier mobility for the Mo(tfd-COCF₃)₃-doped PBTTT was reasonably lower than that for anion-exchanged one. This is because highly-ordered lamellar structure of PBTTT

can be distorted by an introduction of relatively large organo-metallic dopant. The detailed structure has been investigated previously in our study (Fujimoto et al JMCC (2017)).

For the comparison between anion-exchanged sample and TPA-sample (comparison between orange and red curves), the reviewer is also correct that a deeper valence band observed suggests higher doping level for TPA-sample. The increase in doping level can lead directly a 20% increase in conductivity for TPA-sample compared to anion-exchanged sample. To be honest, the correlation between doping level and shift of the Fermi energy is not quantitatively understood at the moment. Assuming the density-of-states (DOS) of neutral PBTTT oligomers, the obtained 1 hole per monomer unit corresponds to 0.88 eV shift in the Fermi energy (see the red line in the attached energy dependent DOS below), which is in agreement with the experimental value for TPA-doped PBTTT (0.8 eV shift). This means that the observed Fermi energy shift reflects the band filling. However, we are skeptical about this calculation because there is no evidence that the rigid band approximation is hold for highly-doped polymers. It is more reasonable to envisage that the band calculation based on the neutral oligomer is violated because the repeat unit is completely cationized. Taking this uncertainty into consideration, the calculated Fermi level shift from anion-exchanged sample to TPA-doped sample is estimated to be 0.13 eV, which is inconsistent with the experimental result (0.2 eV shift). We do not speculate, but merely note that the discrepancy may be due to the violation of rigid band approximation.



In the revised manuscript, we clarified that changes in doping levels were discussed qualitatively from PYS and optical absorption measurements. In addition, we emphasize that there is ambiguity in determining the carrier density and mobility from the Hall effect measurements. It has been

already shown in previous studies by Prof. Vitaly Podzorov that the Hall carrier density and Hall mobility are not accurately determined when carriers are partially localize.

(Reviewer's Comment 3)

Finally, a typo at bottom of page 3: "radial salts" needs to be changed to "radical salts"

(Our Reply 3)

We appreciate the reviewer for pointing out the typo. We revised this, and carefully checked the entire manuscript again.

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Reviewer #2

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We are grateful for the positive evaluation particularly of our experimental results and we have carefully considered his/her suggestions and revised the manuscript accordingly.

(Reviewer's Comment 1)

A remaining question seems to be the role of the radical cation in determining the ultimate morphology. Would other triarylaminers, or other organic acceptors with different structures, be effective? This issue limits the generality of the structure-activity guidance provided by this paper.

(Our Reply 1)

We expect that radical salts of other triarylaminers would also serve as an effective dopant. In our doping process, electron transfer reaction is initiated by the presence of triarylamine radical cations at the surface of polymer thin films. Because the radical cation is not present in the resulting thin films, the doping ability is unlikely to be limited by the morphology. Redox potentials of triarylaminers with various substitutions have been reported (N. G. Connelly and W. E. Geiger, Chem. Rev. 96, 877 (1996)). Among them, triarylaminers with highly anodic redox potentials would serve as a candidate. This would enable one to design stronger or weaker dopants compared to tris(4-bromophenyl)amine based dopants. Other than triphenylaminers, we have confirmed that radical salts of thianthrene derivative also work as the effective dopant (the

manuscript will be submitted elsewhere), which supports generality of our strategy. To make it clear, we added the sentence in p.5.

(Reviewer's Comment 2)

There is a large literature of conducting polymers with conductivities between 100 and 1000 S/cm. This literature and representative values (5-10 additional references, or a couple of reviews that aggregate these data) should be summarized so that the quantitative conductivity enhancements can be evaluated relative to the state of the art.

(Our Reply 2)

The reviewer's comment makes a perfect sense. Due to the space limitation, we summarized the conductivity data from literature in SI.

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Reviewer #3

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We are grateful for the positive evaluation particularly of our experimental results and we have carefully considered his/her suggestions and revised the manuscript accordingly. I

(Reviewer's Comment 1)

Very recently, Segalman, Chabinye, and co-workers published a paper titled "Effects of Counter-Ion Size on Delocalization of Carriers and Stability of Doped Semiconducting Polymers" in Adv. Electron. Mater. (Adv. Electron. Mater. 2020, 2000595). This work also looks at PBTTT and the role of counterions. The authors of this work used the ion exchange method developed by Watanabe and co-workers (Nature, 2019). Many of the results in the Adv. Electron. Mater. Paper are similar to the results presented in this manuscript. The authors may be disappointed to learn about this possible scoop. However, I think that the method to dope conjugated polymers using triarylamine radical cations are still novel. So, I suggest that the authors compare their data and discuss their results in the context of the Adv. Electron. Mater.

(Our Reply 1)

We are grateful for the reviewer's comment, and are aware that Prof. Chabinye has reported the counter-ion effect as well. As the reviewer gave us a credit, our main focus is the development of novel dopant and the analysis of their cocrystal formation. Because the suggested reference is very useful to interpret our results, we added this in the revised manuscript.

(Reviewer's Comment 2)

In the literature, the compound triphenylamine is abbreviated as TPA. Here they are using tris(4-bromophenyl)amine. Perhaps they can use an alternate abbreviation to avoid confusion.

(Our Reply 2)

We agree that our abbreviation for tris(4-bromophenyl)amine was confusing for readers. Following other papers, the abbreviation was changed to TBPA, emphasizing Br substitution in trisphenylamine. According to this change, we modified the figure legends as well.

(Reviewer's Comment 3)

The authors use a free-energy argument for electron transfer, which is OK from a thermodynamic point-of-view. How does the rate of electron transfer change with dopants or anion? The authors need not answer this question but perhaps comment on the reorganization energies for the dopants, which will impact the kinetics. Is F4TCNQ ineffective because of slow electron transfer or because the thermodynamics favor a partial electron transfer?

(Our Reply 3)

We are grateful for the reviewer's comment that should be clarified more. Because the rate of electron transfer is now under investigation, we keep this argument in private communication only to the reviewer. We expect that the rate of electron transfer can be fast enough so that the quasi-equilibrium is reached for all the employed doping conditions in our study. PYS measurements of doped polymer films showed that the resulting IP is close to the redox potential of the employed dopant, which suggests that doping proceeds to quasi-equilibrium state owing to fast electron transfer process. This can apply F4TCNQ doping as well; F4TCNQ-doped polymer film shows IP of 5.2 eV that is also close to the redox potential of F4TCNQ, therefore doping efficiency with F4TCNQ is likely to be limited by the thermodynamics rather than the rate of electron transfer. The Rate of electron transfer is expected to depend on factors such as dopant, semiconductor, solvent, and process temperature, where the reorganization energy of solvated molecules may give a major effect based on the Marcus theory. For this reason, systems with

large solvation energy may suffer from slow electron transfer process as the reviewer anticipates.
We are now investigating the solvation effect.

Editorial changes

List of changes (Main changes are highlighted as a blue text)

References

- References 23, 24 and, 53, in the revised manuscript were added.

Figures

- TPA was modified to TBPA.

6th Jan 21

Dear Professor Watanabe,

Your manuscript titled "Supramolecular cocrystals built through redox-triggered ion intercalation in π -conjugated polymers" has now been seen again by the three referees, whose comments appear below. In light of their advice I am delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Materials under the open access CC BY license (Creative Commons Attribution v4.0 International License).

We therefore invite you to edit your manuscript to comply with our journal policies and formatting style in order to maximise the accessibility and therefore the impact of your work.

EDITORIAL REQUESTS

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Best regards,

John Plummer, PhD
Chief Editor
orcid.org/0000-0003-4824-8497
Communications Materials

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

Although there's still more to be learned, I think the authors have made a reasonable effort to respond to all three referees' comments, and I think their work will stimulate additional research in the field. I recommend publication.

Reviewer #2 (Remarks to the Author):

Questions have been adequately addressed. The paper is now suitable for acceptance.

Reviewer #3 (Remarks to the Author):

The authors have addressed my comments. I am satisfied with the revised manuscript.