

High-efficiency and long-lifetime deep-blue phosphorescent OLEDs using deuterated exciplex-forming host

Corresponding Author: Professor Lian Duan

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This paper by Duan and coworkers reported a deuterated exciplex host for deep-blue phosphorescent OLEDs with EQE up to 27.4% and an operational lifetime (T90) of 370 h at 1000 cd/m², achieving 1.6-fold lifetime improvement. The non-deuterated exciplex hosts were reported by Sun et al. in 2022 (10.1038/s41566-022-00958-4), and this work further deuterated the hosts to improve the operational lifetime in blue OLEDs and investigated the mechanisms of deuteration effect on device degradation. While this study is a nice addition to the deuterated OLED research, I do feel that the novelty and significance of this work are not clearly presented as the deuteration effect of enhancing both the charge transport (10.1002/smsc.202000057) and photochemical stability (10.1021/acsami.2c22882) are previously reported. In addition, some results do not fully support the authors' argument of the underlying mechanism for performance enhancement brought by deuteration. Therefore, the paper is not suitable for publication in Nat. Comm. in the present form. To improve the manuscript, the authors should clearly define its significance and address the specific issues below.

1. The authors' claim of their device lifetime being the longest at this specific color coordinate is kind of a stretch. While it is not technically wrong, the previous paper by Sun et al. already reported a T95 of 150 h using non-deuterated hosts and the same dopant, albeit at a slightly different color coordinate.
2. The authors stated that they only deuterated the carbazole moieties because electronic orbitals are only located on them. While the triazine group in SiTrzCz2 has no hydrogen, the phenyl next to the triazine obviously carries a large portion of the LUMO (line 132). Moreover, the entire aryl silane moiety participated in the HOMO/LUMOs in the ionic states of both hosts. The author should modify their argument.
3. While deuteration can sometimes increase the BDE of C-H bonds, I don't think the minute differences in the calculated BDE for C-N and C-C bonds in deuterated hosts are meaningful (Table S1). I would recommend dropping the argument in line 168-170.
4. Deuteration normally does not change the molecule's steady-state photophysical properties. Why do the deuterated hosts here show "significant" red shifts in PL emissions (line 179-180), which contradicts the claim in line 195-196 that there is a "negligible" effect on radiative processes? The authors need to measure the absorption and emissions of undeuterated hosts under the same conditions and plot them in the same graph for direct comparison, instead of citing literature results.
5. What are the experimental procedure and testing conditions (any encapsulation, testing environment, etc.) for the photostability measurement?
6. The differences in FWHM between deuterated and non-deuterated films and devices are really small. How reproducible are they? Such small differences in EL spectra could be due to various factors, such as the microcavity effect, changes in recombination zone, and batch variation in film thicknesses. Error bars for the shoulder peak height or CIE coordinates are highly recommended.
7. The reduced distance between the donor and the acceptor does not necessarily lead to an increase in the film density. In fact, the density increase (line 240) is purely due to the heavier deuterium (about 2% increase in MW for the hosts used). Note that the extra neutron in deuterium does not change the molecular volume/packing to a meaningful degree. Only less than 1% decrease in crystal unit cell volume was previously observed (10.1002/smsc.202000057).
8. The charge transports of the exciplex are enhanced by deuteration, and the voltages in the single carrier and EL devices were significantly reduced. But why does the device's power efficiency only register marginal improvement given a much-reduced driving voltage? The ageing current in line 296 is in mA. Shouldn't it be in mA/cm²?
9. The lifetime curves are almost linear, even at the very beginning of the ageing process, while the PL ageing test is not linear. The author should discuss it and provide a longer lifetime curve beyond T90.

10. There are some minor grammatical errors and typos, such as "funct" in line 111. Please do a global check.

Reviewer #2

(Remarks to the Author)

The authors synthesize deuterated versions of the blue dopants, SiCzCz and SiTrzCz2, resulting in D-SiCzCz and D-SiTrzCz2, respectively. As expected, both molecular stability and device lifetime have improved while maintaining EQE and λ_{EL} , setting a record for blue phosphorescent OLEDs. However, the Pt complex BD-02 and the host materials, SiCzCz and SiTrzCz2 have been published in Nature Photonics (Nat. Photon. 16, 212–218 (2022)). While this work is sound, from the reviewer's point of view, the only difference between this study and previous report only lies in the deuteration. However, the concept of deuteration to enhance the stability and hence the device lifetime has been reported by Adach and co-workers, and others. Moreover, the reviewer also realizes that the D-carbazoles used in this study were purchased directly. Therefore, the reviewer does not see the importance of this study from angle of both novelty and synthetic challenge, and hence believe that this manuscript is not suitable for publication in Nature Communication. Some comments are listed below.

1. The sentence "the tetraphenylsilane segments maintain the same as they only funct as a nert group..." on page 5 contains an abbreviation. The word "function" should not be abbreviated as "funct."
2. The wavenumber axis of FT-IR is typically arranged from high to low energy, from left to right. However, Figures 1b and 1c are labeled reversely.
3. The λ_{em} of SiCzCz and D-SiCzCz are 387 nm and 377 nm, respectively, while the λ_{em} of SiTrzCz2 and D-SiTrzCz2 are 428 nm and 427 nm. What accounts for the apparent differences between these two materials after deuteration?
4. The absorption spectrum of D-SiCzCz shows a shoulder at 375 nm. However, the absorption spectrum of protonated SiCzCz does not exhibit a similar feature. This has to be clarified.

Reviewer #3

(Remarks to the Author)

This manuscript by W. Yuan et al. discusses how deuterated electron-donor (D) and electron-acceptor (A) components affect the photoluminescence (PL) and electroluminescence (EL) characteristics. The authors illustrate that the deuterated D:A blend film exhibits greater PL and EL stability than its undeuterated counterpart. This marks the first instance of reported positive deuteration effects in D:A blend films utilized in organic light-emitting devices. The paper presents impressive findings on important subjects. Consequently, this reviewer supports its publication in the journal after addressing the following comments.

- 1) The authors suggested that the tighter molecular arrangement in the deuterated D:A blend creates a more rigid environment for emitter molecules (BD-02), leading to a slightly higher PLQY in the 10 wt%-BD-02 doped film than that observed in the undeuterated D:A blend. Since the rigid matrix will suppress molecular vibration modes, the PLQY of the D:A blend itself should exhibit a higher PLQY than that of the undeuterated D:A blend. Please provide the PL data of D:A blends (i.e., without BD-02 dopant).
- 2) The authors noted that "The lowered vibrations could suppress the vibronic coupling between high vibration levels of the ground states and low vibration levels of the excited states, thus favoring the suppression of non-radiative decay for a high PLQY." If non-radiative decay from the excited state of BD-02 is effectively minimized in the deuterated D:A blend, it should extend the phosphorescence lifetime. Nonetheless, the lifetime is still slightly shorter compared to the undeuterated D:A blend. There is inconsistency with the theory. Please comment.
- 3) The authors noted that "the current density of the HODs based on deuterated exciplexes was approaching saturation" on page 12. I could not understand the physical meaning of "saturation". Isn't that just the equipment's measurement limit?
- 4) The electrical-aging measurement in single carrier diodes clearly shows the high stability of the deuterated D:A blend against carrier transport. However, to gain more insight, I recommend adding the electrical-aging measurement in single carrier diodes under photo-excitation.
- 5) Please update the figure caption of Fig. 4(b). Which symbol corresponds to the luminance data? Also, similar to my comment 3, I could not understand the physical meaning of "saturation."
- 6) An exciplex forms following a charge transfer event caused by photo- or electrical excitation. Because the exciplex does not form in a ground state, the words and figure captions (e.g., Fig. 3a, 3b, 3e, 3f) in the manuscript can be considered misleading.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

This work by Duan and coworkers reported deuterated exciplex hosts for deep-blue phosphorescent OLEDs with EQEs up to 27.4% and an operational lifetime (T90) up to 557 h at 1000 cd/m², achieving up to 1.6-fold lifetime improvement over hydrogen hosts. The paper has been revised according to the first-round reviewer comments and has adequately addressed most of the issues raised by reviewers. They also added more device data, achieving better lifetime results using a modified Pt dopant at the expense of efficiencies and color. The author tried to distinguish their work from previous studies by emphasizing the importance of deuterating both the hosts in the exciplex forming system. Yet, the significance and uniqueness of their key findings require further elucidation. The manuscript may still be publishable if the author could further resolve the following concerns.

1. In the revision, the authors have modified their arguments for significance and centered on the “external deuteration effect” on the exciplex-forming host pair. Besides the known advantageous effects brought by deuteration, such as higher photochemical stability, better charge transport and higher efficiencies in triplet devices, this work’s key finding is that the deuteration of the host can also improve the device color purity by reducing the EL spectrum’s shoulder peak. Is this effect unique to the exciplex-forming host and why? What would the EL spectra look like when only one deuterated host (D-SiCzCz or D-SiTrzCz2) is used?
2. The author utilized MD simulations, which show that the deuterated exciplex has more compact packing, to explain the reduced shoulder peak in PL/EL emissions. What will the MD simulation results be for a single host system (D-SiCzCz or D-SiTrzCz2) under the same calculation conditions?
3. The author used another dopant, PtON-tb-DTB, to demonstrate the “external deuteration effect”. A smaller increase of lifetime (1.4x) was achieved. What’s the reason for the less prominent enhancement effect?
4. Although the authors have provided abundant data to show the improvement of color purity as a result of host deuteration, the effect is still minute. How significant will this spectrum change be in actual applications, for example a top-emitting device? The shoulder peak would not matter that much in a top-emitting device with a properly designed microcavity. Will a tiny reduction in the shoulder peak change the color purity of an AMOLED display to a meaningful degree?

Reviewer #2

(Remarks to the Author)

The authors have sufficiently addressed the raised questions and meticulously corrected the typographical errors in their revised manuscript. Furthermore, they have re-elucidated and further emphasized the importance of the unprecedented deuterated exciplex-forming host in enhancing the performance of deep blue emitters, providing a more comprehensive discussion. Consequently, I suggest that the revised manuscript is well-suited for publication in Nature Communications.

Reviewer #3

(Remarks to the Author)

The authors have properly addressed my concerns. I am glad to recommend this work for publication without further revision.

Version 2:

Reviewer comments:

Reviewer #1

(Remarks to the Author)

All concerns have been adequately addressed. The "protonated" in the last sentence of the abstract may be ambiguous. It usually means the addition of protons to a molecule in chemistry. The author may consider using another expression, such as "hydrogen-based". Other than that, the manuscript is in good shape and ready for publication without further revisions.

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Response Letter to Reviewers

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This work by Duan and coworkers reported deuterated exciplex hosts for deep-blue phosphorescent OLEDs with EQEs up to 27.4% and an operational lifetime (T90) up to 557 h at 1000 cd/m², achieving up to 1.6-fold lifetime improvement over hydrogen hosts. The paper has been revised according to the first-round reviewer comments and has adequately addressed most of the issues raised by reviewers. They also added more device data, achieving better lifetime results using a modified Pt dopant at the expense of efficiencies and color. The author tried to distinguish their work from previous studies by emphasizing the importance of deuterating both the hosts in the exciplex forming system. Yet, the significance and uniqueness of their key findings require further elucidation. The manuscript may still be publishable if the author could further resolve the following concerns.

Response: Many thanks for your recognition and constructive comments. We hope that our responses below could address your comments.

1. In the revision, the authors have modified their arguments for significance and centered on the “external deuteration effect” on the exciplex-forming host pair. Besides the known advantageous effects brought by deuteration, such as higher photochemical stability, better charge transport and higher efficiencies in triplet devices, this work’s key finding is that the deuteration of the host can also improve the device color purity by reducing the EL spectrum’s shoulder peak. Is this effect unique to the exciplex-forming host and why? What would the EL spectra look like when only one deuterated host (D-SiCzCz or D-SiTrzCz2) is used?

Response: Thank you for your suggestions.

We propose that this phenomenon is not unique to exciplex-forming hosts but represents a distinct property induced by deuteration. As has been noted, while prior studies have documented deuteration effects in stability enhancement and charge transport optimization, the promotion effect of deuterated hosts on phosphorescent materials reported herein constitutes a novel discovery. This advancement holds significant implications for further improving the performance of deep-blue OLEDs. In order to systematically investigate this phenomenon, we characterized devices based on single-host systems with two phosphorescent complexes PtON-TBBI and PtON-tb-DTB. As shown in Fig. R1a and R1b, the EL spectral shoulder intensity of both devices based on deuterated single donor and single acceptor exhibited a distinct reduction compared to their protonated counterparts. In accordance with the above results, the devices based on PtON-tb-DTB exhibited a similar tendency, further confirming that the suppression of spectral shoulder peaks by deuterated hosts is not restricted to exciplex-forming hosts (Fig. R1c and R1d). It should be emphasized that the selection of deuterated exciplex hosts in this work was not merely attributed to their pronounced suppression of spectral shoulders, but crucially to the balanced carrier transport characteristics enabling prolonged operational stability in deep-blue OLEDs.

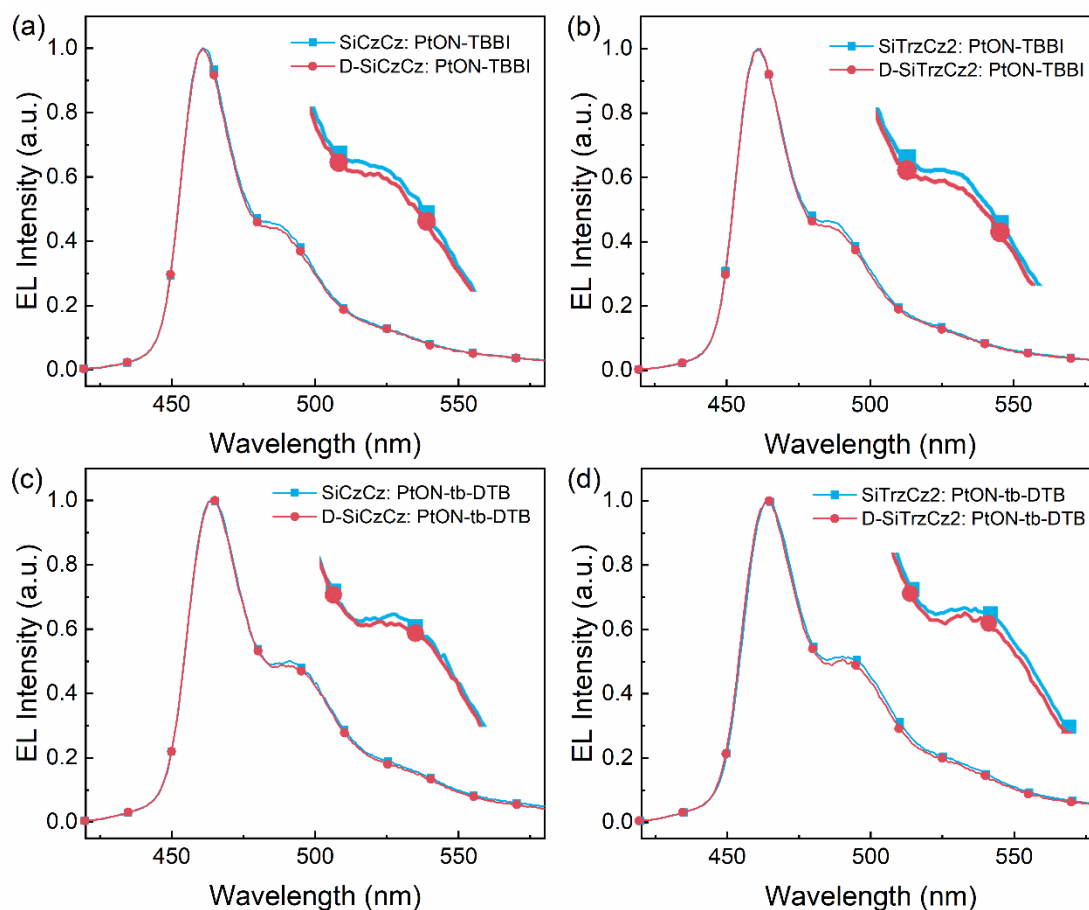


Fig. R1 Normalized EL spectra of the devices based on single-host systems.

2. The author utilized MD simulations, which show that the deuterated exciplex has more compact packing, to explain the reduced shoulder peak in PL/EL emissions. What will the MD simulation results be for a single host system (D-SiCzCz or D-SiTrzCz2) under the same calculation conditions?

Response: Thank you for your suggestions.

We performed molecular dynamic simulation of the single-host systems to compare the molecular packing modes of the deuterated and protonated host materials doping with PtON-TBBI. As illustrated in **Fig. R2**, in single-donor systems, the density increased from 1125.76 kg/m³ for SiCzCz:PtON-TBBI to 1146.16 kg/m³ for D-SiCzCz:PtON-TBBI, accompanied by a decrease in the average distance from 18.516 to 17.354 Å. A comparable trend was observed in the single-acceptor system, with density increasing from 1158.74 to 1185.51 kg/m³ and average distance decreasing from 18.694 to 17.733 Å. The introduction of deuterated hosts into both single-host matrices yielded a notable enhancement in morphological compactness, which aligns well with the observed trends described in the manuscript. These results further corroborated the “external deuteration effect” of deuterated hosts on phosphorescent dopants.

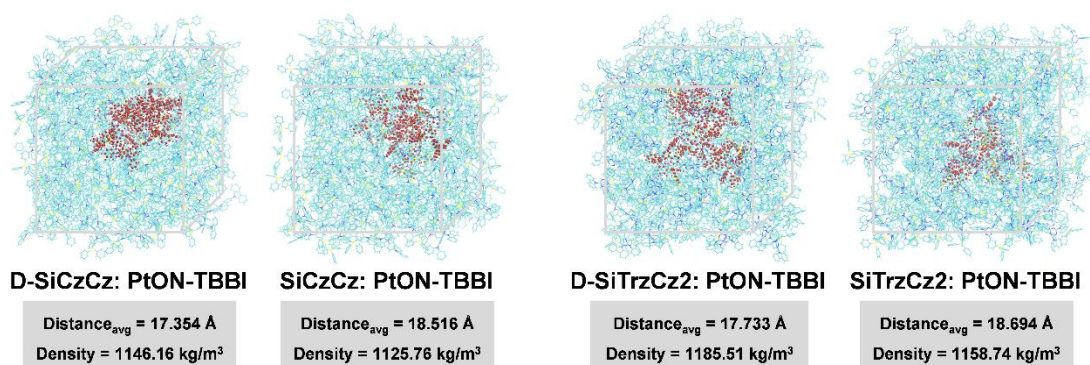


Fig. R2 Molecular dynamic simulation results of single-host systems.

3. The author used another dopant, PtON-tb-DTB, to demonstrate the “external deuteration effect”. A smaller increase of lifetime (1.4x) was achieved. What’s the reason for the less prominent enhancement effect?

Response: Thank you for your suggestions.

The underlying physics on device lifetimes is usually complicated and thus different enhancement effect is reasonable. **The enhanced stability of devices using deuterated hosts could be attributed to, not only the interactions between deuterated hosts and Pt-complexes but also the intrinsic stability of Pt-complexes themselves.** On one hand, owing to the different molecule rigidity and 3D structure of Pt-complexes, the influence of deuterated hosts on molecule packing should be different and thus a different “external deuteration effect”. On the other hand, PtON-tb-DTB has already possessed a better intrinsic stability than BD-02 and thus its stability may be less sensitive to molecule vibrations than BD-02. Other influence could also not be ruled out, for instance, the different charge transporting abilities of Pt-complexes. Though the different ratios, the enhancement on device stability is universal.

4. Although the authors have provided abundant data to show the improvement of color purity as a result of host deuteration, the effect is still minute. How significant will this spectrum change be in actual applications, for example a top-emitting device? The shoulder peak would not matter that much in a top-emitting device with a properly designed microcavity. Will a tiny reduction in the shoulder peak change the color purity of an AMOLED display to a meaningful degree?

Response: Thank you for your suggestions.

It is true that the shoulder peak would be reduced in a top-emitting device with a properly designed microcavity, which would generate a similar color purity. A meaningful improvement for the reduced shoulder peak should be the enhanced device efficiency in top-emitting devices. The top-emitting devices would eliminate the emissions of the shoulders using a designed microcavity, which though improving color-purity but also sacrificing the emitting energy of the shoulders for a reduced device efficiency. With weaker shoulders, the reduces in emitting energy would be also reduced and thus higher device efficiency. That is the reason why a narrowband emission with weak shoulders is highly pursued in this field.

To better elucidate these discrepancies, we conducted an optical simulation by using SETFOS, theoretically predicted the EL spectra of top-emitting devices based on our bottom-emitting ones and the results were shown in Fig. R3. The simulated EL spectra exhibit a marginal narrowing of FWHM values across all systems, ultimately converging to a remarkably value of 15 nm. As

anticipated, spectral analysis reveals that deuterated systems demonstrated only slightly reduced CIE_y coordinates compared with the protonated counterparts. What deserved to be paid more attention is the enhanced device efficiency in terms of blue index (BI), defined as the ratio of current efficiency to CIE_y coordinate, which is the most adopted parameter that evaluate the efficiency of top-emitting devices (*Nat. Photonics* 2021, 15, 208-215). When normalized to the protonated reference system (assigned a BI value of 100), deuterated systems based on PtON-TBBI and PtON-tb-DTB exhibit relative BI increments to 102.5 and 107.5, respectively. It should also be noted that the current BI calculations only derive from spectral difference. If we take into consideration the improved EQEs by deuteration, an even more enhancement in BI value could be anticipated. This systematic investigation further validates the strategic importance of deuteration engineering for achieving high-performance deep-blue electroluminescent devices.

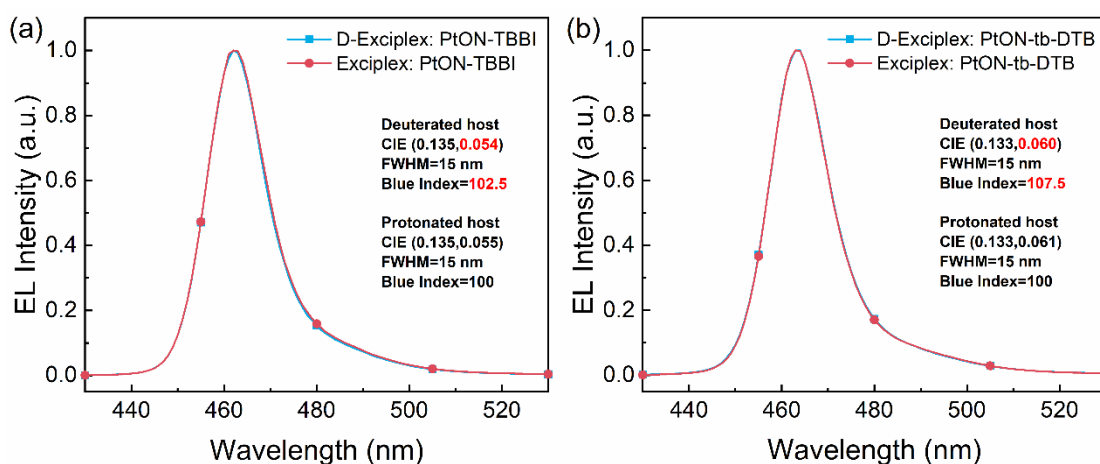


Fig. R3 Simulated EL spectra of the top-emitting devices based on (a) PtON-TBBI and (b) PtON-tb-DTB.

Reviewer #2 (Remarks to the Author):

The authors have sufficiently addressed the raised questions and meticulously corrected the typographical errors in their revised manuscript. Furthermore, they have re-elucidated and further emphasized the importance of the unprecedented deuterated exciplex-forming host in enhancing the performance of deep blue emitters, providing a more comprehensive discussion. Consequently, I suggest that the revised manuscript is well-suited for publication in Nature Communications.

Response: Thank you for your recognition and support of our work.

Reviewer #3 (Remarks to the Author):

The authors have properly addressed my concerns. I am glad to recommend this work for publication without further revision.

Response: Thank you for your recognition and support of our work.

Response Letter to Reviewers

Reviewers' comments:

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All concerns have been adequately addressed. The "protonated" in the last sentence of the abstract may be ambiguous. It usually means the addition of protons to a molecule in chemistry. The author may consider using another expression, such as "hydrogen-based". Other than that, the manuscript is in good shape and ready for publication without further revisions.

Response: Thank you for your recognition and support of our work. We have changed the expression in the abstract.