Durham Research Online

Deposited in DRO:
09 April 2021

Version of attached file:
Published Version

Peer-review status of attached file:
Peer-reviewed

Citation for published item:
Colella, Marco and Danos, Andrew and Monkman, Andrew P. (2019) 'Less Is More: Dilution Enhances Optical and Electrical Performance of a TADF Exciplex.', Journal of physical chemistry letters., 10 (4). pp. 793-798.

Further information on publisher's website:
https://doi.org/10.1021/acs.jpcllett.8b03646

Publisher's copyright statement:
This document is the Accepted Manuscript version of a Published Work that appeared in final form in Journal of physical chemistry letters, copyright © American Chemical Society after peer review and technical editing by the publisher. To access the final edited and published work see https://doi.org/10.1021/acs.jpcllett.8b03646.

Use policy

The full-text may be used and/or reproduced, and given to third parties in any format or medium, without prior permission or charge, for personal research or study, educational, or not-for-profit purposes provided that:
- a full bibliographic reference is made to the original source
- a link is made to the metadata record in DRO
- the full-text is not changed in any way

The full-text must not be sold in any format or medium without the formal permission of the copyright holders.

Please consult the full DRO policy for further details.
Less Is More: Dilution Enhances Optical and Electrical Performance of a TADF Exciplex

Marco Colella, Andrew Danos, and Andrew P. Monkman

Department of Physics, Durham University, South Road, Durham DH1 3LE, United Kingdom

Supporting Information

ABSTRACT: A surprising yet highly practical approach to improve the performance of a TADF exciplex blend is reported. Using the TSBPA donor and PO-T2T acceptor to form an exciplex, we are able to blue shift the emission, increase PLQY from 58 to 80%, and increase the device EQE from 14.8 to 19.2% by simply diluting the exciplex with an inert high triplet energy host material—here either UGH-3 or DPEPO. These effects are explained in terms of an increasing donor–acceptor distance and associated charge separation, while different behaviors observed in the different hosts are attributed to different energy barriers to electron transfer through the host. We expect that the observed performance-enhancing effects of dilution will be general to different exciplex blends and host materials and offer a new way to optimize the electrical properties of exciplex emission layers with narrow blue emission.

In recent years, organic light-emitting diodes (OLEDs) based on thermally activated delayed fluorescence (TADF) have attracted much attention. Efficient TADF has been observed in both intermolecular (exciplex) and covalently linked (molecular) charge transfer (CT) systems. At present, reports investigating new structures, color tuning methods, and strategies for improving device performance of TADF molecules greatly outnumber similar reports for exciplexes. Nonetheless, existing studies show the potential of TADF exciplexes as high-performance emitters or triplet harvesting systems, resulting in nonexponential decay kinetics and time-dependent emission spectra. While the donor (D) and acceptor (A) spacing is rigidly set by the chemical structures of molecular TADF materials, D–A spacing in exciplexes has only gained limited attention as a design parameter until recently. Adachi et al. recently reported that inserting a spacer layer between an interfacial blue exciplex and orientation are to the singlet and triplet energies in an

© 2019 American Chemical Society

Published: February 6, 2019

Received: December 5, 2018

Accepted: February 6, 2019

DOI: 10.1021/acs.jpclett.8b03646
J. Phys. Chem. Lett. 2019, 10, 793−798
with dilution in both hosts up to 2.85 eV in 90 vol % UGH-3 and 2.80 in 90 vol % DPEPO. In both 90% host films (i.e., exciplex highly diluted), TSBPA emission becomes clearly visible at wavelengths below 425 nm, indicating that exciplex formation is being hindered; however, it is extremely surprising that the exciplex is still so dominant even diluted at 90 vol % host.

We assign the blue shift of the exciplex emission onset, $\hbar \nu_{\text{max}}$, to the increase in the average D–A separation distance as the host vol % increases. Increasing the average D–A distance and therefore the separation, $r$, of the electron and hole in the CT state causes the Coulombic potential energy, $E_C(r)$, to rise (toward zero) as per eq 1. The average distances between nearest-neighbor D–A pairs has also been estimated in Table 1, using the molecular masses and volume fractions of the films and assuming a uniform cubic lattice, uniform orientation distribution, and density of 1.1 g/mL (approximated from tetraphenylsilane) for all materials.14,15 The total

| dilution | vol % | average D–A distance (Å) | $\tau_{\text{DF}}$ (μs) | PL onset (eV) | PL fwhm (eV) | PLQY air/N2 |
|----------|-------|--------------------------|--------------------------|--------------|--------------|--------------|
| neat exciplex | 0 | 6.0 | 2.4 ± 0.1 | 2.67 | 0.51 | 0.45/0.58 |
| UGH-3     | 10   | 6.3 | 2.2 ± 0.1 | 2.68 | 0.72 | 0.50/0.63 |
| UGH-3     | 30   | 6.8 | 2.8 ± 0.1 | 2.70 | 0.51 | 0.51/0.65 |
| UGH-3     | 50   | 7.6 | 3.1 ± 0.1 | 2.79 | 0.58 | 0.67/0.80 |
| UGH-3     | 70   | 9.0 | 3.1 ± 0.2 | 2.83 | 0.58 | 0.49/0.70 |
| UGH-3     | 90   | 13  | 2.85       | 0.35/0.35 |
| DPEPO     | 10   | 6.3 | 2.4 ± 0.1 | 2.67 | 0.52 | 0.52/0.68 |
| DPEPO     | 30   | 6.8 | 2.5 ± 0.1 | 2.67 | 0.34/0.45 |
| DPEPO     | 50   | 7.6 | 2.3 ± 0.1 | 2.70 | 0.23/0.28 |
| DPEPO     | 70   | 9.0 | 2.9 ± 0.1 | 2.73 | 0.28/0.38 |
| DPEPO     | 90   | 13  | 2.8 ± 0.1 | 2.80 | 0.06/0.07 |
indeed known to be a very polar host,16 while UGH-3 is largely polarities. Rich in polar O

which are, respectively, the permittivity of the vacuum and of the medium.

Figure 3. (a) PLQY of vacuum-deposited films in air and nitrogen atmospheres with different dilution in UGH-3 and DPEPO. (b) Schematic representation of the D (blue), A (black), and host (gray) HOMO and LUMO levels relevant to electron transport (blue arrows) and exciplex formation (green oval).

energy of the CT state thus increases with separation (eq 2), resulting in a higher-energy exciplex and emission, in accordance with the findings of Al’Attar12 and calculations reported by Kim et al.9 This observation is also consistent with previously mentioned recent work of Adachi et al.10

\[ E_C(r) = -\frac{e^2}{4\pi\varepsilon_0 \varepsilon_r F r} \]

\[ h\nu_{\text{max}} \approx I_D - A_A - E_C \]  

where \( e \) is the electron charge, \( F \) is the electric field, and \( \varepsilon_0 \) and \( \varepsilon \) are, respectively, the permittivity of the vacuum and of the medium. \( I_D \) and \( A_A \) are the ionization potential of the donor and the electronic affinity of the acceptor. The electric field term in eq 1 has the effect of broadening the CT emission band as the field increases.12

The difference in the magnitude of the observed blue shift between the two hosts is rationalized in terms of their different polarities. Rich in polar O–C and O=P bonds, DPEPO is indeed known to be a very polar host,16 while UGH-3 is largely aromatic and nonpolar.13 Increased host polarity allows the exciplex CT state to relax further (by shielding the coulomb term through increased \( \varepsilon \)) before emission, resulting in a consistently smaller overall blue shift for DPEPO films than for UGH-3. The sensitivity of the exciplex emission to polarity even at high dilutions suggest that the exciplex maintains CT character even at the largest D–A distances examined here.16

To better understand how the presence of a host affects the kinetics of charge separation, exciplex formation, and emission, time-resolved PL decays of these films were measured and are shown in Figures S4–S6. The spectra at different times all display the same blue shift with dilution seen in Figure 2, while films of TSBPA in DPEPO or UGH-3 (without PO-T2T) show no sign of exciplex formation (Figure S9), confirming the inert nature of the hosts. Delayed fluorescence (DF) decay times (\( \tau_{\text{DF}} \)) were obtained for the different exciplex samples by fitting the experimental data with monoexponential decay functions in the second cascade region of the log–log intensity time plots. A general increase in \( \tau_{\text{DF}} \) was observed with increasing dilution for both hosts, with values given in Table 1. The increase in delayed lifetime can be indicative of a decrease in nonradiative decay from the exciplex triplet state, although this explanation cannot be asserted from lifetimes alone. The dependence of the delayed emission intensity upon excitation power was also checked for each sample (Figures S7 and S8) in order to confirm that the DF was due to TADF rather than triplet fusion.

To better understand the cause of the observed increase in \( \tau_{\text{DF}} \), we measured the absolute PLQYs of the films, shown in Figure 3a and Table 1. We note that at the excitation wavelengths used (340 nm for PLQY, 355 nm for time-resolved PL) we only excite the exciplex donor. For all films, the PLQY was found to increase with removal of atmospheric oxygen, confirming that triplet harvesting is occurring. For the UGH-3 diluted films, we observed that the PLQY increased from 58% for the neat exciplex to a maximum of 80% when diluted with 50 vol % UGH-3.

The PLQYs then decreased when the exciplex was further diluted. We assign this decrease to the fact that at very high dilution (and corresponding large D–A distances) the probability of exciplex formation must begin to decrease, so that eventually most of the excitons remain localized on the donor and therefore decay through low-efficiency pathways. This is supported by the growth of the 340 nm TSBPA donor emission band at high dilutions in Figure 2, as well as the fact that at 90% dilution the PLQYs in air and vacuum converge, indicating negligible contribution to emission from TADF. This is also seen in the time-resolved spectra, where a higher ratio of overall prompt (containing both exciplex and donor contributions) to delayed emission (exciplex only) is seen in higher-dilution time-resolved PL traces (Figures S5 and S6). This changing ratio of prompt to delayed emission manifests as an apparent lower level of DF when delayed time points are measured with initial time points.

Combined, the tandem increases in \( \tau_{\text{DF}} \) and PLQY with dilution strongly suggest that some concentration quenching pathways are reduced for exciplexes with larger D–A distances. This observation may also indicate that PLQY is enhanced.
through reduction in the degree of charge separation in the excited state, for example, avoiding nonradiative radical ion pair formation.\textsuperscript{18,19} Despite the fact that the PL emission onsets blue shift upon dilution closer to the TSBPA and PO-T2T triplet energies (2.9 and 3.0 eV, respectively),\textsuperscript{13} we nonetheless rule out the possibility that the increase in PLQY arises from a distance-associated minimization of $\Delta E_{ST}$ (and improvement of triplet harvesting) as this would accelerate rISC, leading instead to a shorter $\tau_{DF}$.\textsuperscript{7}

Surprisingly, the trend in PLQY shown for the UGH-3 diluted exciplex is not reproduced for those diluted in DPEPO. Instead, the PLQY has an initial increase up to 68\% for the 10 vol % (similar to what was measured for the sample diluted with 10 vol % UGH-3) but only decreases upon further dilution. The difference in optical behavior for different hosts demonstrates that the CT state formation in the diluted films must be mediated by the host as a tunneling or purely through-space mechanism would be independent of the choice of host. Furthermore, from the estimated $D^{-A}$ separations, it is clearly seen that electron transfer (ET) occurs strongly at separations greater than 0.6 nm, which again indicates that the host is acting as a mediator between the LUMO orbitals of TSBPA ($-2.3$ eV\textsuperscript{18}) and PO-T2T ($-3.2$ eV\textsuperscript{19}). As pictured in Figure 3b, the differences in the LUMO levels of the hosts then readily explain why the UGH-3 spacer (LUMO $-2.8$ eV\textsuperscript{17}) still allows exciplex formation and high PLQY at larger distances whereas DPEPO (LUMO $-2.0$ eV\textsuperscript{3}) does not.\textsuperscript{21,22}

Comparing the fwhm for the CT emission band as a function of UGH-3 dilution (Table 1), we observe an increase as the dilution increases, until 90\% UGH-3 where it instead narrows. This might imply that only certain orientations of D and A facilitate enhance hopping ET through the intermediate host molecule. The broadened spectra result from a distribution of emitting CT states having different conformations and ET routes,\textsuperscript{21} and at 90\% dilution, only the highly blue-shifted and narrowed exciplexes can form. This then gives an indication of a possible way to produce narrow emission bands from exciplex systems. We again stress that in all photophysical measurements only the donor is excited, so that ET through the host is required for exciplex formation in the diluted films. This is not the case for electrical excitation where the CT state is formed directly from free charges, as discussed in the context of OLEDs below.

We estimate the distance dependence of ET by plotting the ratio of residual donor emission to exciplex emission from the spectra in Figure 2 (normalizing for changes in exciplex PLQY upon dilution). For UGH-3, we find an exponential increase in donor emission with average D–A spacing (Figure S9D), from which we estimate a distance decay constant $\beta = 1.1$ Å\textsuperscript{-1}, indicating efficient hopping ET with similar distance dependence as that found in other organic systems.\textsuperscript{22} For DPEPO, the mechanism for long-range ET cannot proceed exothermically and is not yet understood, but based on the PLQY rolloff, it is not as efficient as that in UGH-3.

To assess the practical application of the dilution-enhanced exciplex, OLEDs with different host vol % DPEPO and UGH-3 were produced. The structure used was NPB (40 nm)|TSBPA (10 nm)|TSBPA:PO-T2T 1:1 in X vol % Host (40 nm)|PO-T2T (50 nm)|LiF (1 nm)|Al (100 nm), where X was varied from 0 to 70 vol %. In both device series, the maximum EQE (shown in Figure 4a,c) increases with dilution up to 50 vol %, matching the trend seen for UGH-3 film PLQYs in Figure 3a. The maximum device brightness decreases with increasing dilution as this reduces the total amount of exciplex D and A in the device. The electroluminescence (EL) spectra of both UGH-3 (Figure 4b) and DPEPO (Figure 4d) OLEDs blue shift with dilution, consistent with the trend observed in the steady-state PL spectra (Figure 2), although the EL spectra are each slightly red-shifted with respect to their PL counterparts. This red shift of EL compared to PL is commonly seen in TADF systems and is likely due to the differences between direct charge carrier recombination to form the CT state in

---

**Figure 4.** EQE vs brightness and EL spectra of OLEDs with different dilution vol %, respectively, in UGH-3 (a,b) and DPEPO (c,d).
devices, compared to photoexcitation, and ET to form the CT state in photophysics.\textsuperscript{20−}

In Figure 5a, we compare the values of the maximum measured EQE for the devices produced with estimated based on the PLQYs using $\eta = \eta_{\text{out}} \cdot \eta_{\text{fr}} \cdot \gamma$, where $\eta_{\text{out}}$ is the outcoupling factor (assumed here to be 0.25), the PLQY values taken from Table 1 are those from the UGH-3 samples, $\gamma$ is the charge balance factor (assumed to be 1), and $\eta_{\text{fr}}$ is the fraction of excited states that can radiatively decay, which is 1 for TADF exciplexes that can harvest both singlets and triplets. We use the UGH-3 PLQYs here, having identified that DPEPO blocks ET and exciplex formation after optical excitation. In contrast, in electrically driven devices, there is no need for ET through the diluting host material, as shown schematically in Figure 5b. As such, we did not expect to observe the same early decrease in DPEPO device EQEs as was observed for PLQYs.

Indeed, the estimated EQE values in Figure 5a are in very good agreement with the measured maximum EQE values for both UGH-3 and DPEPO based devices for dilution up to 30 vol %. At 50 vol % dilution, the UGH-3 device still shows very good agreement with an estimated EQE of 20% and a measured one of 19.2% (the highest measured EQE in this study, and a 20% enhancement of the neat exciplex), while the DPEPO device qualitatively follows the estimated trend but quantitatively underperforms. At higher dilutions, the maximum EQE decreases, again in line to what was observed for PLQYs and again thought to be due to extreme D−A distances inhibiting exciplex formation.

It is not trivial to explain the discrepancy between the estimated EQEs and those measured in hosts at 50 vol % and above. This might be caused by the different polarities and dielectric constants of DPEPO and UGH-3, large values of which would electrostatically screen the donor and acceptor, reducing their coupling and the probability of exciplex formation. If this is the case, significant care must be taken to choose appropriate hosts for future studies in exciplex dilution. Similar to the requirements for molecular TADF hosts, these hosts will need to balance both polarity and electrical transport properties to achieve the best devices.

Alternatively, it could be that the discrepancy is a simple problem of charge balance in these specific devices and that further optimization of the organic stack could increase efficiency closer to the estimated values. Nonetheless, both device series and the estimates show the same qualitative trend.

In conclusion, we diluted the exciplex formed by TSBPA and PO-T2T into two different hosts with different polarity. Rather than immediately preventing exciplex formation, we found that dilution blue shifts the emission of the exciplex due to the reduction of the electrostatic interaction between the CT state’s D and A over greater distances. The exciplex maintains strong CT character despite the D−A separation, with films diluted in DPEPO systematically red-shifted compared to those in UGH-3 due to the effect of polarity on CT state relaxation. In addition to the emission blue shift, we demonstrated an increase in the PLQY of the exciplex passing from 58 to 80% before further dilution began to hinder exciplex formation. The increase in PLQY is directly transferable to OLEDs, where the maximum EQE increases from 14.8% for the neat exciplex to 19.2% for the device diluted with 50 vol % UGH-3, in good agreement with the estimated EQE values.

Our attribution of these effects to simple increases in D−A distance and reduction in concentration quenching suggests that the performance-enhancing effects of dilution are likely to be general to other exciplex blends and host materials. Optimization of exciplex dilution—previously assumed to only inhibit exciplex formation—will likely allow exciplex based TADF devices to rapidly match and exceed the performance of leading molecular TADF materials.

\section*{ASSOCIATED CONTENT}

\section*{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b03646.

Experimental methods; absorption spectra of PO-T2T, TSBPA, and neat and diluted exciplex films; time-resolved emission decays, spectra, and DF power dependences of neat and diluted exciplexes; time-
resolved emission decays and spectra of TSBPA in DPEPO or UGH-3 hosts showing no exciplex formation in the absence of PO-T2T, and distance dependence of residual donor emission (PDF)

■ AUTHOR INFORMATION

Corresponding Authors
*E-mail: andrew.danos@durham.ac.uk.
*E-mail: a.p.monkman@durham.ac.uk.

ORCID

Marco Colella: 0000-0003-1627-2978
Andrew Danos: 0000-0002-1752-8675
Andrew P. Monkman: 0000-0002-0784-8640

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors would like to acknowledge the EXCILIGHT and HyperOLED projects funded by the European Union’s Horizon 2020 Research and Innovation Programme under Grant Agreements No. 674990 and No. 732013.

■ REFERENCES

(1) Uoyama, H.; Goushi, K.; Shizu, K.; Nomura, H.; Adachi, C. Highly Efficient Organic Light-Emitting Diodes from Delayed Fluorescence. *Nature* 2012, 492, 234–238.
(2) dos Santos, P. L.; Dias, F. B.; Monkman, A. P. Investigation of the Mechanisms Giving Rise to TADF in Exciplex States. *J. Phys. Chem. C* 2016, 120, 18259–18267.
(3) dos Santos, P. L.; Ward, J. S.; Bryce, M. R.; Monkman, A. P. Using Guest–Host Interactions To Optimize the Efficiency of TADF OLEDs. *J. Phys. Chem. Lett.* 2016, 7, 3341–3346.
(4) dos Santos, P. L.; Ward, J. S.; Batsonov, A. S.; Bryce, M. R.; Monkman, A. P. Optical and Polarity Control of Donor – Acceptor Conformation and Their Charge-Transfer States in Thermally Activated Delayed-Fluorescence Molecules. *J. Phys. Chem. C* 2017, 121, 16462–16469.
(5) Higginbotham, H. F.; Yi, C.; Monkman, A. P.; Wong, K. Effects of Ortho-Phenyl Substitution on the RISC Rate of D–A Type TADF Molecules. *J. Phys. Chem. C* 2018, 122, 7627–7634.
(6) Zhang, Q.; Li, B.; Huang, S.; Nomura, H.; Tanaka, H.; Adachi, C. Efficient Blue Organic Light-Emitting Diodes Employing Thermally Activated Delayed Fluorescence. *Nat. Photonics* 2014, 8, 326–332.
(7) Dias, F. B.; Bourdakos, K. N.; Jankus, V.; Moss, K. C.; Kamtekar, K. T.; Bhalla, V.; Santos, J.; Bryce, M. R.; Monkman, A. P. Triplet Harvesting with 100% Efficiency by Way of Thermally Activated Delayed Fluorescence in Charge Transfer OLED Emitters. *Adv. Mater.* 2013, 25, 3707–3714.
(8) Kim, K.-H.; Yoo, S.-J.; Kim, J.-J. Boosting Triplet Harvest by Reducing Nonradiative Transition of Exciplex toward Fluorescent Organic Light-Emitting Diodes with 100% Internal Quantum Efficiency. *Chem. Mater.* 2016, 28, 1936–1941.
(9) Moon, C.-K.; Huh, J.-S.; Kim, J.-M.; Kim, J.-J. Electronic Structure and Emission Process of Excited Charge Transfer States in Solids. *Chem. Mater.* 2018, 30, 5648–5654.
(10) Nakano, T.; Itoh, H.; Furukawa, T.; Morimoto, K.; Adachi, C. Long-Range Coupling of Electron-Hole Pairs in Spatially Separated Organic Donor-Acceptor Layers. *Sci. Adv.* 2016, 2, e1501470–e1501470.
(11) Graves, D.; Jankus, V.; Dias, F. B.; Monkman, A. Photophysical Investigation of the Thermally Activated Delayed Emission from Films of M-MTDATA: PBD Exciplex. *Adv. Funct. Mater.* 2014, 24, 2343–2351.
(12) Al Attar, H. A.; Monkman, A. P. Electric Field Induce Blue Shift and Intensity Enhancement in 2D Exciplex Organic Light Emitting Diodes; Controlling Electron-Hole Separation. *Adv. Mater.* 2016, 28, 8014–8020.
(13) Chapran, M.; Pander, P.; Vasyliova, M.; Wiosna-Salyga, G.; Ułanski, J.; Dias, F. B.; Data, P. Realizing 20% External Quantum Efficiency in Electroluminescence with Efficient Thermally Activated Delayed Fluorescence from an Exciplex. *ACS Appl. Mater. Interfaces*; Under Revision.
(14) Aesar, A. Density of Tetrphenylsilane. https://www.alfa.com/en/catalog/L04857/ (accessed Feb 1, 2019).
(15) Davis, N. J. L. K.; MacQueen, R. W.; Roberts, D. A.; Danos, A.; Dehn, S.; Perrier, S.; Schmidt, T. W. Energy Transfer in Pendant Perylene Diimide Copolymers. *J. Mater. Chem. C* 2016, 4, 8270.
(16) Reed, L. H.; Allen, L. C. Bond Polarity Index: Application to Group Electronegativity. *J. Phys. Chem.* 1992, 96, 157–164.
(17) Gordon, M. *The Exciplex*, 1st ed.; Academic Press, 1975.
(18) Huang, H. M.; Pham, T. B. Van; Graimpp, G.; Kattnig, D. R. Exciplexes versus Loose Ion Pairs: How Does the Driving Force Impact the Initial Product Ratio of Photoinduced Charge Separation Reactions? *J. Phys. Chem. Lett.* 2014, 5, 3188–3194.
(19) Lin, T.-C.; Sarma, M.; Chen, Y.-T.; Liu, S.-H.; Lin, K.-T.; Chiang, P.-Y.; Chuang, W.-T.; Liu, Y.-C.; Hsu, H.-F.; Hung, W.-Y.; et al. Probe Exciplex Structure of Highly Efficient Thermally Activated Delayed Fluorescence Organic Light Emitting Diodes. *Nat. Commun.* 2018, 9, 3111.
(20) Yook, K. S.; Lee, J. Y. Organic Materials for Deep Blue Phosphorescent Organic Light-Emitting Diodes. *Adv. Mater.* 2012, 24, 3169–3190.
(21) Natali, M.; Campagna, S.; Scandola, F. Photoinduced Electron Transfer across Molecular Bridges: Electron- and Hole-Transfer Superexchange Pathways. *Chem. Soc. Rev.* 2014, 43, 4005–4018.
(22) Wenger, O. S. Photoinduced Electron Tunneling between Randomly Dispersed Donors and Acceptors in Frozen Glasses and Other Rigid Matrices. *Phys. Chem. Chem. Phys.* 2013, 15, 10673–10685.
(23) Dinnocenzo, J. P.; Feinberg, A. M.; Farid, S. Multiple Intermolecular Exciplexes in Highly Polar Solvents. *J. Phys. Chem. A* 2017, 121, 3662–3670.

DOI: 10.1021/acs.jpcl.8b01646
*J. Phys. Chem. Lett.* 2019, 10, 793–798