ChemPubSoc Europe
DOI: 10.1002/open.201500214
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ChemistryOPEN
Communications

Opposite Anisotropy Effects of Singlet and Triplet Exciton Diffusion in Tetracene Crystal

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We observe the diffusion anisotropy difference between singlet and triplet excitons in organic crystals; that is, singlet and triplet excitons may have completely different spatial direction preference for diffusion. This phenomenon can be ascribed to the distinct dependence of different excitonic couplings (Coulomb Förster vs. exchange Dexter) existing in singlet and triplet excitons on their intermolecular distance and intermolecular orientation. Such a discovery provides insights for understanding the fundamental photophysical process in a vast range of organic condensed-phase systems and optimizing the efficiency of organic optoelectronic materials.

The diffusion of excitons (excited state with a bound electron-hole pair) is well known as one of the key steps in the photophysical process for a vast range of problems from biophysics (photosynthetic systems) to materials science (optoelectronic devices).[1–9] Very useful insights on exciton diffusion can be obtained by direct spatial, temporal, and spectral observation of exciton transport, as illustrated recently and remarkably by Akselrod et al.[10] and Huang et al.[11] Akselrod et al. concluded from the anisotropy of triplet exciton diffusion that most of the excitation energy transport in crystalline tetracene is due to exciton hopping instead of photon emission followed by reabsorption (ERA),[12] and Huang et al. revealed a new and promising cooperative singlet/triplet transport mechanism for tetracene excitons. Although the anisotropy for exciton diffusion on organic crystals has been known for around fifty years,[13,14] the correct interpretation for anisotropy of the exciton transport in organic optoelectronics is not trivial.[4,10,15–20] Nevertheless, such anisotropic feature is usually considered to be able to provide rational design rules for more efficient organic solar cells (OSCs) by an optimal utilization of exciton diffusion at specified spatial directions.

Akselrod et al.'s recent discussion[10] about the anisotropy was successfully devoted to the difference between the triplet exciton diffusion in the *ab* plane and that along the *c* axis, and the reason of the more delicate but vital difference between the *a* axis and *b* axis is still unclear. Moreover, it is generally assumed that diffusions for singlet and triplet exciton have the same preferential direction[11] although this will be speculated by this work. The accurate interpretation of the experiment on exciton diffusion is further complicated by the fact that the exciton diffusion process involves not only that of triplet excitons with long lifetimes but also that of the initially photogenerated singlet excitons with short lifetimes, and the singlets and triplets can be converted from each other via singlet fission or pair fusion.[5,11,21–28] An accurate theoretical description of exciton diffusion and its anisotropy feature is obviously crucial for understanding the fundamental photophysical mechanism in natural biological systems and providing guidelines for optimal power conversion efficiency (PCE) in OSCs. The aim of this work is therefore to answer a specific fundamental question during the complicated exciton diffusion processes: do singlet and triplet excitons diffusion have different anisotropy?

It is well-known that singlet and triplet excitons undergo different excitation energy transfer (EET) mechanisms; that is, Förster energy transfer[29] is the dominant mechanism for singlets, and Dexter energy transfer[30] is the dominant mechanism for triplets. Such two different mechanisms of exciton transfer (Förster vs. Dexter) can have distinct dependencies on the intermolecular distance and orientation because the Förster mechanism is mainly contributed by the Coulomb coupling, while the Dexter mechanism is contributed by only the exchange interaction. This would potentially result in the different (or even opposite) anisotropic exciton transport behaviors for singlets and triplets, but it has not been reported yet. In this study, we aim to determine whether singlet and triplet exciton diffusion have different anisotropy in organic crystals by using first-principles quantum chemical calculations in conjugation with kinetic Monte Carlo (KMC)[31] random walk simulations. Herein all our calculations and simulations were performed for a typical and active organic semiconductor, crystalline tetracene,[32] which was the chief material used in historical studies of singlet fission.

Considering the exciton transfer rate is largely determined by the electronic couplings between excitons localized at different neighboring molecules, we first evaluated the exciton couplings within four representative dimer structures (Figure 1 a) by virtue of first-principles time-dependent density functional theory (TDDFT)[33] calculations. (see S1 in the Supporting Information for the detailed methodology). Table 1 shows our results for the coupling calculation.

In general, the magnitudes of triplet exciton couplings are not surprisingly much smaller than those for singlets as shown in Table 1, because triplet energy transfer involves an exchange

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Supporting information for this article can be found under http://dx.doi.org/10.1002/open.201500214.

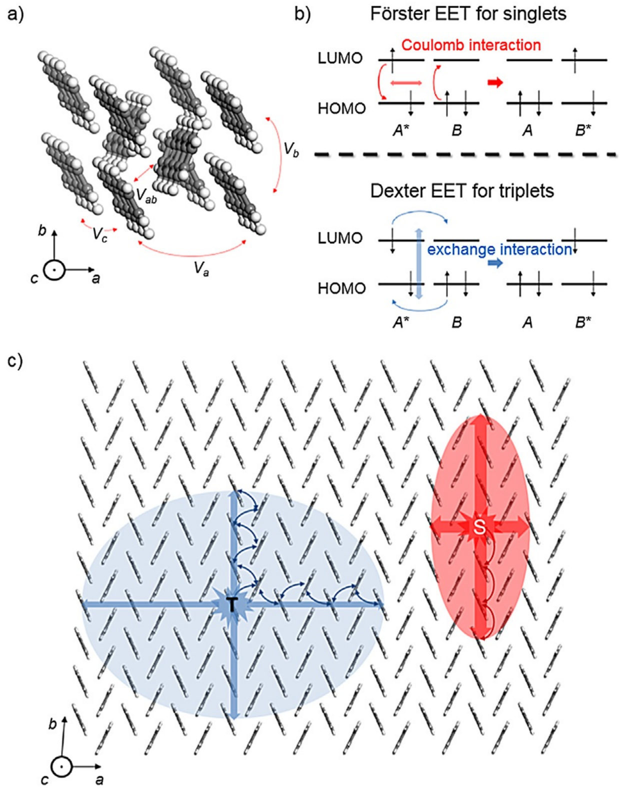

Figure 1. An overview of this study: a) four different exciton couplings in tetracene crystal structure; b) two different transport mechanisms; c) scheme of the opposite anisotropy for the transport of singlet (red) and triplet (blue) excitons. The dominating hopping modes for both singlet and triplet are shown using double-headed arrows.

Table 1. The intermolecular distance (d) and exciton couplings for singlets ($|V_s|$) and triplets ($|V_\tau|$) in four representative dimers.

Direction	d [Å]	$\lvert V_s\rvert$ [meV]	$\lvert V_\tau\rvert$ [meV]
a	7.98	12.61	0.0
b	6.14	41.85	1.2
ab	5.15	27.51	7.2
C	13.57	4.91	0.1

of two electrons of different spins, and only the minor exchange interactions contribute to triplet exciton couplings.[34] The magnitude of exchange coupling, the dominant term for triplet exciton coupling, relies on the overlap of the wavefunctions of the two exciton states and consequently is more sensitive to the intermolecular distance instead of the intermolecular orientation.[17,35,36] As a consequence, among all the triplet exciton couplings, the absolute value of V_{ab} became largest because its intermolecular distance d between the centers of mass (COMs) of the two molecules is shortest as illustrated in Table 1. For singlet exciton coupling, the Coulomb interaction becomes dominant and is determined by not only the distance but also the angle between two transition dipoles as a second-order dipole–dipole interaction,[17,37]

$$V_{ij} = \frac{1}{4\pi\varepsilon}\left[\frac{\vec{\mu}_i \cdot \vec{\mu}_j}{r^3} - 3\frac{\left(\vec{\mu}_i \cdot \vec{r}_{ji}\right)\left(\vec{\mu}_j \cdot \vec{r}_{ij}\right)}{r^5}\right] \tag{1}$$

in other words, the singlet exciton coupling depends on not only the intermolecular distance but also the intermolecular orientation, differing from the triplet exciton coupling which mainly depends only on intermolecular distance. V_{ab} has the shortest intermolecular distance, but it has two nonparallel interacting transition dipoles. As a result, V_{ab} is not largest for singlet exciton couplings, but instead V_b becomes the largest one due to its parallel alignment and moderate intermolecular distance. In brief, from Table 1 we notice that singlet excitons have the largest couplings along the *b* direction, while triplet excitons have the largest couplings along the *ab* direction.

According to the magnitudes of the exciton couplings illustrated in Table 1, the exciton diffusion should be much faster in the *ab* plane than in the *c* direction for both singlets and triplets, which was also verified by the recent experiment[10] by Akselrod et al. So in the following, we will only focus on the exciton diffusion in the *ab* plane by performing a two-dimension random walk KMC simulation with exciton transfer rate evaluated by Marcus theory.[38] (see S2 in the Supporting Information for the detailed methodology)

To measure the exciton diffusion length L, we used the equation $L=\sqrt{2D\tau}$, in which D is the determined diffusion coeffcient from KMC simulations with 20 000 trajectories for each simulation, and τ is the lifetime of the exciton. Here we adopted the experimental values for exciton lifetime $\tau = 0.15$ ns[39] and 1.37 µs[10] for singlet and triplet excitons, respectively.

The calculated average (analysis using all KMC trajectories) diffusion coeffcient D is $4.11\times10^{-7}\,\mathrm{m^2\,s^{-1}}$ for singlet excitons, much larger than that for triplet excitons, $1.35\times10^{-8}\,\mathrm{m^2\,s^{-1}}$, because of the much larger exciton couplings for singlet excitons as illustrated in Table 1. However, the triplets have significantly longer life times than the singlets by four orders of magnitude, 1.37 µs vs. 0.15 ns. As an overall consequence, our calculations predicted that in tetracene crystals, triplets still have an average diffusion length of 0.193 µm—longer than singlets which have L of 11.10 nm agreeing well with the experimental finding (by fluorescence spectrum)[40] of 12 nm (average value). Our prediction of the diffusion length L for triplet exciton, 0.193 µm, is also consistent with the experimental results (from delayed fluorescence spectrum fitting), 0.79/0.61 µm (for the *a*/*b* axis),[10] on the order of magnitude.

We then further investigated the directional preference of the exciton diffusion for both singlets and triplets. Figure 2 shows our calculated diffusion coefficient and diffusion length results for singlet and triplet excitons at all spatial directions on the *ab* plane. The results clearly indicate that the exciton diffusion of both singlets and triplets are anisotropic, but their preferred directions are quite different. For singlet exciton diffusion, the largest distribution is the hopping in the *b* direction because they have the largest exciton couplings in the *b* direction as illustrated in Table 1. From Table 1, one may also notice that, although triplet excitons have negligible couplings in the *a* direction, their dominant coupling terms are in the ab direc-

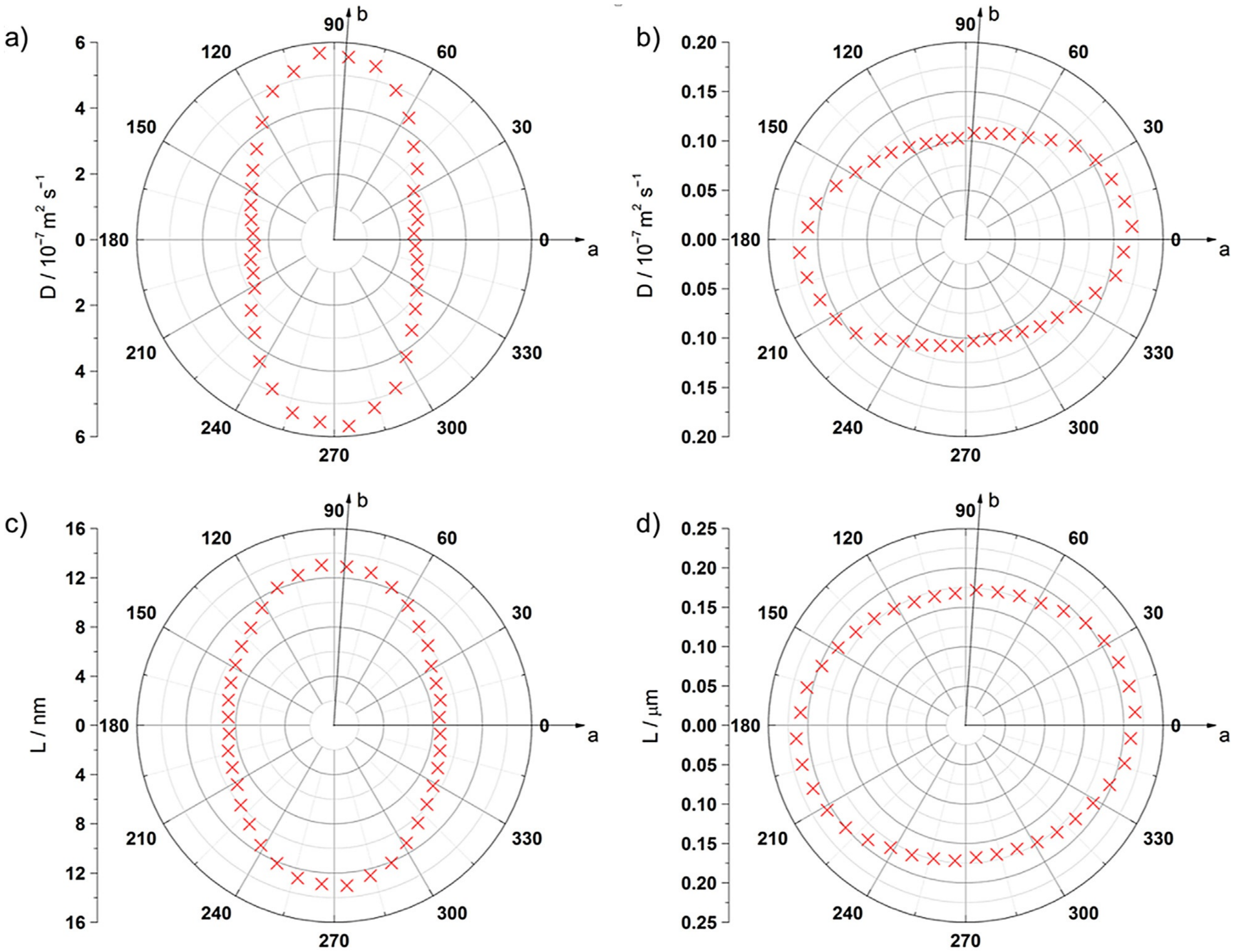

Figure 2. Anisotropy behavior of exciton diffusion on the *ab* plane: a) singlet exciton diffusion coefficient; b) triplet exciton diffusion coefficient; c) singlet exciton diffusion length; d) triplet exciton diffusion length.

tion with V_{ab}:$V_b \approx 6$. Because the direction of such a hopping mode between nonparallel neighbor molecules is closer to the direction of the *a* axis than the *b* axis, the exciton diffusion occurs more likely in the *a* direction than the *b* direction. This result nicely explains the recent experimental finding of the anisotropic triplet exciton diffusion in ordered tetracene solids by Akselrod et al.[10] Our determined D_b:D_a for triplets is 1:1.45—very close to their experimental finding of 1:1.69; and the ratio for singlets is 1:0.428, also close to another experimental result of 1:0.304 by Huang, et al.[11] More importantly, for the first time we found that singlets and triplets have completely opposite anisotropy effects for exciton diffusion in tetracene crystals; that is, the preferred diffusion direction is the *b* direction for singlets but the *a* direction for triplets. This finding is in contrast to the common assumption[11] that singlets and triplets have the same preferred spatial direction during the diffusion process. Obviously, such anisotropy differences may have potential utilization in future for designing new smart devices with optoelectronic signals in different spatial directions at different time scales.

In the above parts, our simulations were based on a perfect tetracene crystal without any disorder, which might be not the case in actual devices.[41–52] The exciton coupling, a key electronic structure parameter in our kinetic simulations, has been reported to owe a broadening in realistic materials due to the molecule position disorder.[41,53–57] Van Voorhis et al.'s recent theoretical simulation[17] indicated that the diffusion constant and diffusion length of triplet excitons are robust to disorder-induced coupling broadening. Here, we further examined the thermal fluctuation effect of exciton coupling on the singlet exciton diffusion and its anisotropy by using classical molecular dynamics (MD) simulation to generate a large number of thermal-fluctuated examples for the broadening statistics. (see S3 in the Supporting Information for the detailed methodology) Table 2 reports our results for the broadening σ (standard deviation) and average couplings, which are very close to the values without thermal fluctuation in Table 1. Although V_{ab} has a relatively large fluctuation, the dominant V_b still has very small broadening. Therefore, one can expect that the thermal fluctuation effect will not significantly change the exciton diffusion picture.

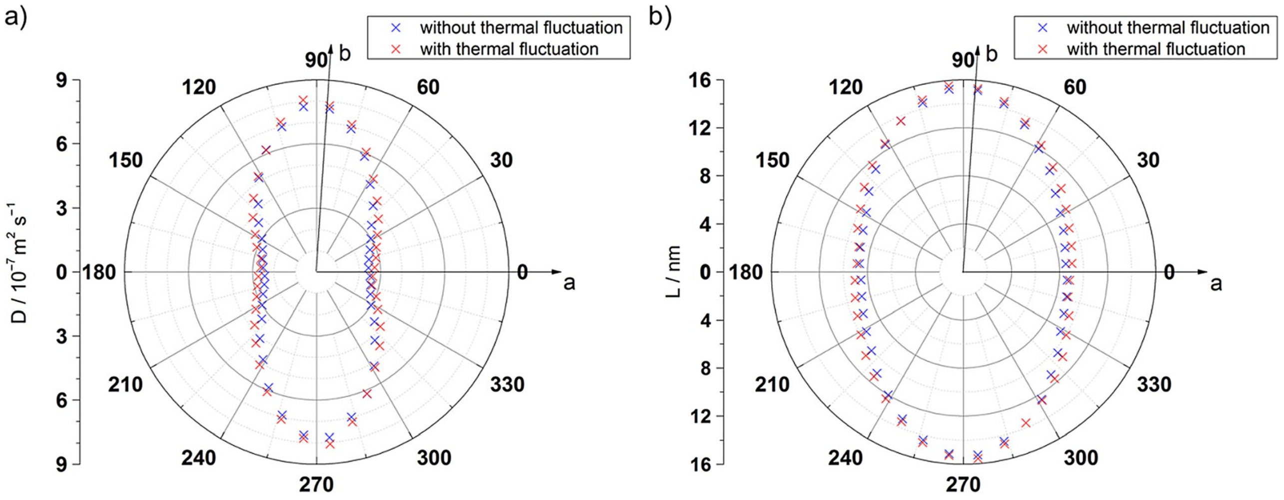

Figure 3. Thermal fluctuation effect for singlet exciton transport on the *ab* plane: a) comparison of singlet exciton diffusion coefficients with and without thermal fluctuation effect; b) comparison of singlet exciton diffusion lengths with and without thermal fluctuation effect.

Table 2. Singlet exciton couplings with thermal fluctuation effect.

Direction	Average value [meV]	σ
a	13.33	2.48
b	50.44	9.63
ab	26.73	10.50
c	5.21	1.05

σ: Broadening; standard deviation.

Figure 3 illustrates the comparison of singlet exciton diffusions with and without thermal fluctuations. We can see that there are only very marginal differences between the cases with and without thermal fluctuations. There are very small increases of diffusion length *L* in all directions in the case with disorder, but the largest increase in the direction of the *a* axis is only 0.4 nm, which is much less than the total diffusion length. Consequently, we may conclude that the thermal fluctuation effect will not alter the anisotropy feature of the singlet exciton diffusion in realistic regime with limited disorder. This is similar to the calculation results by Van Voorhis et al.[17] for triplet excitons. It is also of course worth noting that the role of disorder will be important for more incoherent transport or if the fluctuation is very large in noncrystal materials, but such cases are outside the scope of this study. Anyway, the opposite anisotropy effect for singlet and triplet exciton diffusion can be expected to hold on in practical crystal devices under room temperature.

To summarize, using tetracene as an archetype molecular crystal, we find singlet and triplet exciton diffusions have completely different spatial direction preferences through the combination of quantum chemical calculations and kinetics random-walk simulations. Exciton diffusion is shown to be much weaker in the *c*-direction than within the *ab*-plane in singlet and triplet cases. Furthermore, the exciton diffusion length ratio between the *a* and *b* directions is about 0.4 for singlet excitons and 1.5 for triplet excitons. Initially the excitation energy will diffuse rapidly (but only for a short lifetime) as a singlet exciton diffuses? preferentially along the *b* direction, and then it will diffuse slowly as one (or two) triplet exciton (but for a longer lifetime) preferentially along the *a* direction. The actual diffusion is the convolution of the two processes, and our results are essential for the correct interpretation of the experiment on exciton diffusion, which is made difficult by the different anisotropy of the two processes. Such a novel feature of opposite anisotropy effects can be ascribed to the mechanism difference of singlet and triplet exciton transport (Coulomb Förster vs. exchange Dexter). Thermal fluctuation effect is also shown to have vanishing influence on the anisotropy of the exciton diffusion. Our results enlighten the possibility of designing new efficient and/or smart organic optoelectronic devices by rationally controlling the morphology of donor/acceptor heterojunctions to achieve the full utilization of both singlet and triplet excitons.

Experimental Section

Information about theoretical methods and calculation details can be found in the Supporting Information.

Acknowledgements

The work is supported by the National Natural Science Foundation of China (Grant No. 21373109).

Keywords: anisotropy · exciton diffusion · optoelectronics · organic solar cells · tetracene

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Received: November 23, 2015