

Engineering highways for excitons

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Summary

The distance that excitons can travel is a key parameter for organic photovoltaic materials. In the August issue of *Science Advances*, Sneyd and colleagues report a breakthrough in increasing exciton diffusion length to 300 nm by using highly ordered nanofibers. This approach can enable simpler and more stable solar cells.

Organic photovoltaics have made remarkable progress in recent years with small research solar cells now reaching 19% efficiency, and several companies demonstrating large area installations of lightweight and flexible solar modules for outdoor and indoor power generation.^{1,2} The absorption of light in organic semiconductors leads to the formation of strongly bound electron-hole pairs (excitons). Charge generation then requires an additional step in which excitons travel to a heterojunction between electron donor and acceptor materials where they can dissociate into free charge carriers. Excitons can reach the heterojunction by diffusion, whilst in some cases a direct Förster resonance energy transfer between electron donor and acceptor also contributes.³ The simplest device structure would be a donor layer on top of an acceptor layer (or vice versa) but unfortunately these layers would need to be at least 100 nm thick to absorb light effectively, whilst excitons typically diffuse only about 30 nm or less.⁴ Only the excitons formed within their diffusion length L_D of the heterojunction can generate charge carriers limiting the fraction of light that can be harvested in a planar heterojunction of materials with a short L_D (Figure 1a). One way of overcoming this problem is to blend donor and acceptor materials to form a so-called bulk heterojunction with donor and acceptor domains smaller than L_D (Figure 1b). There are tens of thousands of papers studying such structures. Besides exciton harvesting, such heterojunctions have to support dissociation of bound electron-hole pairs at donor-acceptor interfaces and their extraction to the electrodes. The optimum nanoscale morphology of the bulk heterojunction is difficult to reproduce on a large scale and often lacks long-term stability.

An alternative approach is to increase the exciton diffusion length beyond the absorption length and so improve light harvesting in planar heterojunctions (Figure 1c). Recently, exciton diffusion lengths up to 45 nm have been reported in fused-ring electron acceptors.⁵⁻⁷ These new materials have boosted the performance of planar heterojunctions leading to solar cells with 14% power conversion efficiencies.⁸ These cells showed slower degradation under heating and light soaking than the bulk heterojunctions devices, generating even more interest in materials with long exciton transport.

Writing in the August issue of *Science Advances*, Sneyd et al. report that thin films made of self-assembled nanofibers show long range order and remarkably high exciton diffusion length of 300 nm.⁹ They used living self-assembly of molecularly dissolved amphiphiles to prepare nanofibers. These amphiphiles are made of the 30 repeat unit poly(3-hexylthiophene) terminated with phosphonium borate (P3HT₃₀-[PPh3Me][BPh4]). They formed well-ordered nanofibers in solution by π - π stacking of conjugated P3HT chains (Figure 2). The phosphonium groups stabilized the nanofibers by introducing electrostatic repulsion between them. These nanofibers were deposited on glass or other substrates by drop-casting which produced films consisting of a dense, randomly orientated mesh of nanofibers stacked atop each other. Despite random orientation, these nanofibers exhibited long straight sections of about 80 nm indicating parallel alignment of conjugated P3HT chains to one another over this length. The authors measured the time-resolved expansion of the radial exciton distribution by probing ground state bleaching of P3HT chromophores in optical microscope, and used the speed of expansion in the time range from 10 to 30 ps to determine the diffusion coefficient, D . The value of 1.1 cm²/s obtained is two orders of magnitude higher than values previously reported in spin-coated films of regio-regular P3HT. Assuming that this high exciton diffusivity persists over the entire singlet exciton lifetime of 400 ps, suggests an impressive diffusion length of 300 nm in the nanofibers, implying they act as a highway for excitons.

Many factors contribute to the enhancement of D . First, the energetic disorder is much lower in nanofibers. The width of the exponential absorption edge (the Urbach energy) in nanofibers is just 29 meV and comparable to the thermal energy at room temperature. Low disorder is confirmed by much smaller relaxation energy of excitons by diffusion in nanofibers as compared to spin-coated P3HT films (~70 meV vs 140 meV, respectively, measured as the red-shift of the 0-1 vibronic of the emission peak). Second, the baseline absorbance below the bandgap is very low in nanofibers (<0.001), indicating very low density of deep trap states. These factors, however, are not sufficient to explain the very high D values reported. The authors carried out nonadiabatic molecular dynamics simulations, including long-range dipole-dipole interactions between conjugated P3HT chains. Averaging over many trajectories showed that excitons are mostly localized on a single P3HT chain. However, individual trajectories indicated that, because of the continuous energy exchange with vibrational modes, for a very short time an exciton can be promoted to slightly higher-energy states where its wavefunction is spread over several neighboring P3HT chains. The delocalized exciton can then localize on a different chain and so propagate over several chains in a very short time span. Sneyd et al. stress that long-range dipole-dipole interactions between chromophores and the absence of deep energetic traps are essential for transient delocalization and fast exciton propagation. Further calculations show the importance of extended π -conjugation of P3HT chains for transient delocalization.¹⁰ Longer conjugation leads to weaker nearest-neighbor interactions and hence smaller exciton bandwidth which makes delocalized states thermally accessible from localized states at room temperature.

Transient delocalization under equilibrium conditions proposed by Sneyd et al. provides a new perspective on understanding exciton and charge carrier transport in organic materials. The initial results are very encouraging, however, we would like to see further

experimental verification of the values of D obtained. Imaging of exciton distribution is a very attractive tool to visualize diffusion but it requires high excitation fluence, such as the $4 \mu\text{J}/\text{cm}^2$ used in his work. At this fluence excitons are generated in close proximity to each other, leading to exciton-exciton annihilation (EEA). Because the exciton decay rate by EEA scales quadratically with exciton density, fast EEA at the peak of the excitation spot quickly flattens the exciton distribution leading to its broadening and overestimation of D values. Sneyd et al. acknowledged the artificial expansion by EEA at early times after excitation and argued that its effect is negligible in the time range from 10 to 30 ps. However, this is difficult to reconcile with the fluence-dependent decays of transient absorption and time-resolved photoluminescence, including in the 10-30 ps time range. Because of this non-negligible EEA contribution, the reported D and L_D numbers should be considered as the upper bounds. Sneyd et al. analysed EEA in transient absorption measurements assuming one-dimensional diffusion model and estimated D in the range of 0.3 to 0.5 cm^2/s from it. This analysis, however, did not include contribution from static annihilation without diffusion which is expected because of the spectral overlap of exciton emission with photoinduced absorption and long-range dipole-dipole interactions. In any case, it would be desirable to verify diffusion parameters by other techniques, such as incorporating exciton sensors or quenchers at the end of nanofibers. If confirmed, transient delocalization in highly ordered materials could be a powerful tool for enhancing exciton (and possibly charge) transport in a range of organic optoelectronic devices, and lead to efficient and stable planar organic photovoltaics.

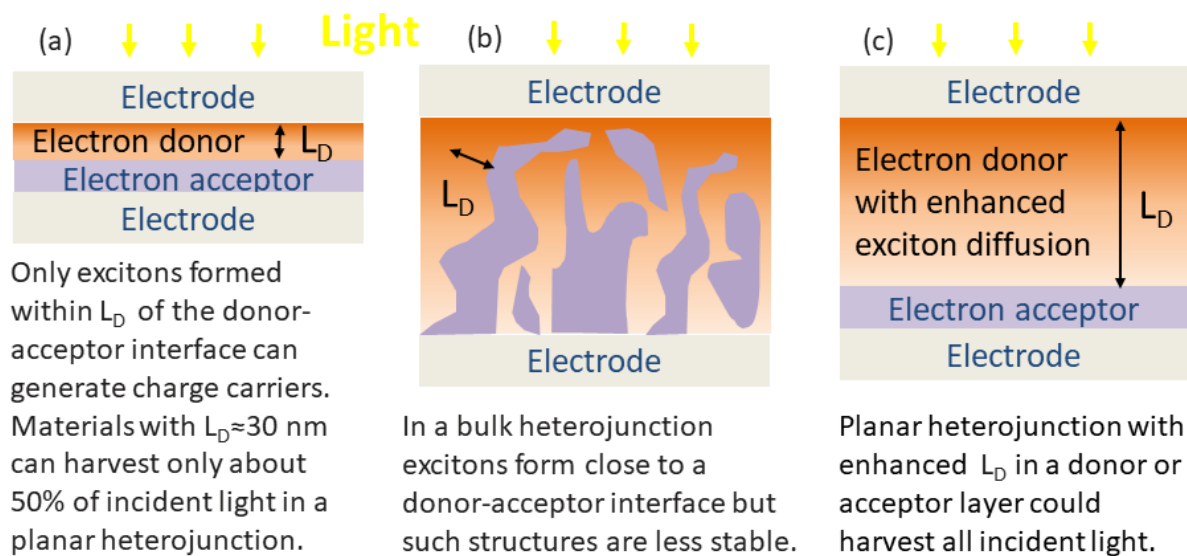


Figure 1. Exciton diffusion length L_D defines the useful thickness of donor and acceptor layers in planar heterojunctions (a, c) and the maximum size of donor and acceptor domains in bulk heterojunctions (b).

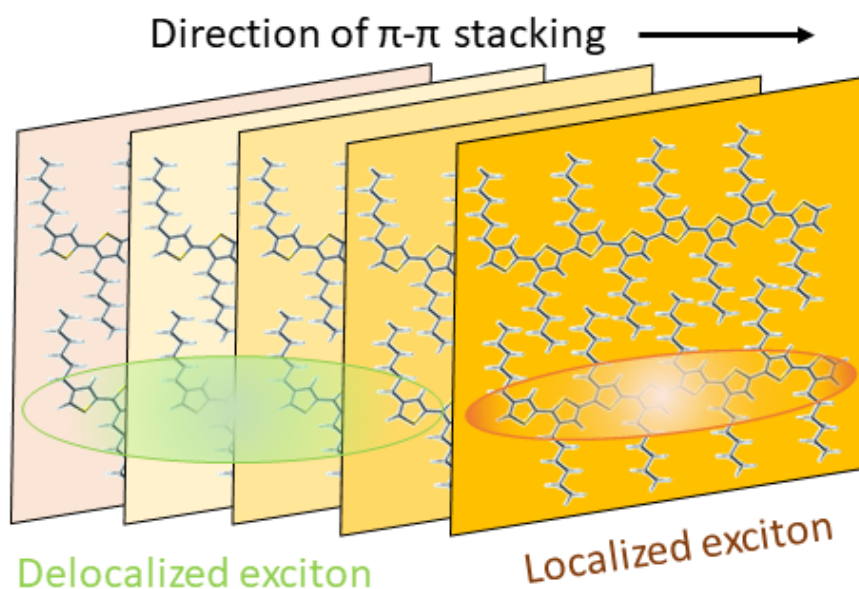


Figure 2. Sneyd et al. report very fast exciton diffusion in thin films made of self-assembled nanofibers where P3HT chains are aligned parallel to one another along the direction of π - π stacking. The authors consider that energy exchange with vibrational modes allows localized excitons to temporarily re-access spatially extended delocalized states where excitons can propagate much faster than by incoherent hopping.

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