

Long singlet exciton diffusion length in organics: quest for ppm pure materials

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Exciton diffusion is an important fundamental process controlling the performance of organic solar cells. In heterojunction donor-acceptor organic solar cells, photogenerated excitons should diffuse to the donor-acceptor interface during their lifetime to dissociate there into free carriers, electrons and holes. Typically, the singlet exciton diffusion length in organics is below 10 nm, which forces using the bulk heterojunction concept instead of a much simpler planar heterojunction. However, in organic semiconductor single crystals the exciton diffusion length can be much longer due to their high structural order. For example, early work on anthracene single crystals reported the singlet exciton diffusion about 60 nm [1], which is comparable to the light absorption length. Therefore, using single crystals in organic solar cells with long exciton diffusion lengths would be highly beneficial.

In this presentation, factors limiting the exciton diffusion length in organics are addressed. As materials, fluorescent organic semiconductor single crystals based on various conjugated

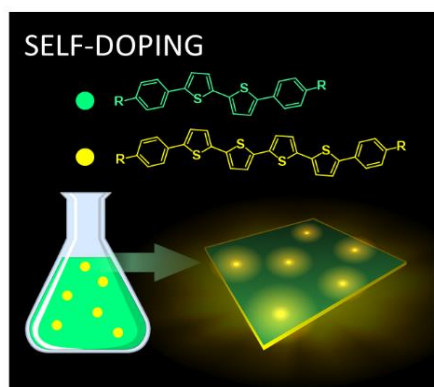


Figure 1. Illustration of molecular self-doping of host by higher emissive self-dopants (yellow dots).

oligoarylenes (thiophene-phenylene, furan-phenylene co-oligomers, etc.) were studied. The singlet exciton diffusion length measured mainly by volume photoluminescence (PL) quenching technique was found to be limited by the material purity [2,3]. Specifically, molecular self-dopants (impurities appearing in the course of chemical synthesis) with concentration down to the ppm level were established to strongly influence the fluorescence in single crystals. In some crystals, as illustrated in Fig. 1, the molecular self-dopants are emissive, and they were used as reporters of exciton trapping. In the purest single crystals of furan-phenylene co-oligomers, the singlet exciton diffusion was about 25 nm [3], whereas the self-dopant can strongly limit it down to a few nanometers.

All of the oligomers studied were synthesized via various Pd-catalyzed cross-coupling reactions (Suzuki, Kumada, and Stille) usually used for synthesis of conjugated materials. In these reactions, the formation of byproducts due to ligand exchange within the organometallic catalytic cycle results in molecular self-dopants with longer conjugation lengths as minor byproducts.

It might well be possible that unintentional doping by longer oligomers also occurred in numerous earlier luminescent studies in nominally chemically pure (>99%) solid samples of conjugated oligomers synthesized via metal-catalyzed cross-coupling reactions. As shown in Refs [2,3], the self-dopant even at low content (<1%) in the host material could strongly affect its luminescent properties. This may be one of the reasons for poor understanding of the luminescent properties of conjugated materials as a very minute concentration of self-dopants can be sufficient to drastically change the luminescence of conjugated oligomers in the solid state.

If the self-dopant is low-emissive, it may quench luminescence of the material via host-dopant energy transfer limiting the exciton diffusion length and resulting in non-radiative losses of excitation energy. Accordingly, molecular self-doping can be detrimental in materials for organic photovoltaics, where a long exciton diffusion length is a prerequisite for high performance of organic solar cells. For an efficient planar heterojunction organic solar cell, one needs to have the singlet exciton diffusion length comparable to the light absorption length, l . For strongly absorbing organics, l is typically about 50 nm, and taking the intermolecular distance as $a=0.5$ nm, one needs to have no more than $\sim(a/l)^3=1$ ppm concentration of exciton traps to avoid their impact on the solar cell performance.

However, such a high level of material purity is a challenge. Indeed, the accuracy of standard techniques used to prove the purity of organic materials (NMR, HPLC, GPC, elemental analysis and mass-spectroscopy) might miss such minor byproducts; therefore, the effect of these tiny-amount molecular self-dopants on the luminescent properties of the nominally chemically pure materials can be largely overlooked in the past. According to Ref. [2,3], the self-dopant molecules are embedded in host crystal matrix substituting the host sites, i.e., the host and dopant form co-crystals. Despite much less solubility of the self-dopants in organic solvents as compared to the host, the self-dopant does not precipitate during self-doping, but it is incorporated in the host crystal. This can be explained by complex formation between the dopant and host molecules already in solution as both have the similar rod-like molecular structures so that they stick together with their molecular axes having nearly the same orientation. These complexes survive in the course of further processing including co-crystallization so that the dopant substitutes the host sites in the host crystal lattice. As a result, complete purification of the host from the dopant is a very complicated task. Moreover, to control of material purity at the ppm level, one needs extremely sensitive methods. Among them, optical methods seem to be the most promising, specifically PL and photothermal spectroscopy methods are discussed.

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