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Transient analysis of triplet exciton dynamics in amorphous organic semiconductor thin films

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Abstract

We study triplet exciton diffusion in the archetype organic material 4,4′-bis(*N*-carbazolyl)biphenyl (CBP) commonly used as a conductive host in the emissive zone of organic light emitting devices. Using time-resolved spectral decay ensuing from the diffusion of an initially localized triplet population to a spatially separated phosphor doped region, we model the delayed fluorescence and phosphorescence decays based on non-dispersive triplet transport. Fits to the model yield a diffusion coefficient of $D = (1.4 \pm 0.3) \times 10^{-8}$ cm^2/s, and a triplet–triplet bimolecular quenching rate constant of $K_{TT} = (1.6 \pm 0.4) \times 10^{-14}$ cm^3/s. The results are extended by doping a wide energy-gap molecule into CBP that serves to frustrate triplet transport, lowering both the diffusion coefficient and annihilation rate. These results are used to model a recently demonstrated white organic light emitting device that depends on triplet diffusion in CBP to excite spatially separate fluorescent and phosphorescent doped regions of the emissive layer. We determine the extent to which diffusion contributes to light emission in this structure, and predict its performance based on ideal lumophores with unity quantum yield.

Keywords: Exciton; Electrophosphorescence; Organic light emitting device; Triplet; Diffusion

1. Introduction

Energy transport by exciton diffusion in organic thin films plays a significant role in many practical applications, including organic light emitting devices [1,2] (OLEDs), and organic photovoltaic cells [3]. For example, Sun et al. recently introduced a white light emitting device that depends on diffusive energy transport to achieve the desired color balance at high luminous efficiency [4]. Exciton diffusion also controls the performance of organic photovoltaics, linking exciton generation to the subsequent dissociation into a free electron and hole at a nearby donor/acceptor interface [3]. In both of these examples, efficient energy transport is required to achieve high device performance.

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The diffusive characteristics of spin singlet and triplet excitons are considerably different. The forbidden triplet exciton decay transition typically takes 10^6 times longer than the allowed singlet decay of 1–10 ns [5]. This leads to a triplet diffusion length >100 nm [6,7] in amorphous organic thin films that is often an order of magnitude larger than for singlets [8,9]. Triplet excitons thus provide a means for efficient energy transport within an organic solid. For example, intersystem crossing following photon absorption in C_{60}-based organic solar cells is a source of triplets that leads to an exciton diffusion length (~40 nm) that is comparable to the optical absorption length [3], resulting in a high device efficiency.

Control of exciton diffusion is the basis for the white-emitting fluorescent/phosphorescent (F/P) hybrid OLED architecture recently reported by Sun et al. [4]. That device uses the different diffusive characteristics of singlet and triplet excitons to spatially separate the decay channels for each species. In constraining singlet decay to a blue fluorescent zone and triplet decay to spatially remote red and green phosphorescent regions, high efficiency white emission was observed. In principle, this device concept offers a lower operating voltage and a more stable white emission spectrum with drive current than conventional all-phosphorescent white organic light emitting devices (WOLEDs), while maintaining the possibility for 100% internal quantum efficiency. Improved understanding of the diffusive process in such a device is one motivation for this current study.

Diffusion also plays an important role in both energy transport and triplet–triplet (T–T) annihilation [5,10], both of which are central to understanding the operation of practical devices. Several studies have examined triplet diffusion in organic molecular crystals [5]. Focus has also been given to thin films by employing both steady-state [7] and time-of-flight experiments under electrical excitation [11]. The simple experimental procedure and easily interpretable results presented here serve to complement these previous investigations.

We employ optically pumped pseudo-time-of-flight measurements to obtain both the triplet diffusion coefficient, D, and the T–T annihilation rate, K_{TT}, for the commonly used OLED host material, 4,4′-bis(*N*-carbazolyl)biphenyl (CBP). These measurements use the delayed fluorescence from CBP and the delayed phosphorescence from a phosphor-doped "sensing layer" to monitor the evolution of the triplet spatial profile. In addition, we demonstrate that the diffusion coefficient is decreased by doping into CBP a wide energy-gap molecule that scatters triplets and frustrates their transport. The results are employed to understand the mechanisms that control the performance of fluorescent/phosphorescent WOLEDs, and to determine the limitations of such an architecture using CBP as a host material.

In Section 2 we develop a theory describing triplet exciton migration and annihilation processes. Experimental details are given in Section 3, and in Section 4 we present the results from transient measurements. In Section 5 we fit and discuss these results in terms of the theory in Section 2, and in Section 6 these results are used to analyze the fluorescent/phosphorescent WOLED. Section 7 provides a summary.

2. Theory

Intermolecular triplet transfer is fundamentally different from that for singlets. Transfer of a singlet exciton is often dominated by long-range (~5 nm) Förster dipole–dipole coupling [9]; however, this mechanism contributes negligibly to triplet transfer since both donor and acceptor transitions are disallowed. Triplets, instead, transfer by the short range (<1 nm) Dexter process [12], an exchange coupling between nearest-neighbor molecules that is permitted by a simultaneous interchange of spin on both the donor and acceptor molecules. Triplet migration thus proceeds as a series of incoherent hops between adjacent molecules that have considerable intermolecular electronic orbital overlap. Both Förster and Dexter processes are modeled as diffusive in the continuum limit [9].

The morphological disorder present in an amorphous organic solid leads to a distribution of both molecular site energies and intersite exchange couplings [13,14]. This results in an inhomogeneously broadened density of states (DOS) within which triplet transport occurs. Relaxation of triplets into the low-energy tail of this DOS gives rise to dispersive transport [13,14], which is typically described by a time-dependent diffusion coefficient. At room temperature, however, thermal energy is generally sufficient to ensure that equilibrium is rapidly approached [14]. Thus, transport quickly moves from the dispersive to the classical regime, at which point it can be described by a time-independent diffusion coefficient.