Effects of optical interference and energy transfer on exciton diffusion length measurements in organic semiconductors

Shawn R. Scully and Michael D. McGehee[a)]
Department of Materials Science and Engineering, Stanford University, Stanford, California 94305-2205

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Exciton diffusion is of great importance to the future design of high efficiency organic photovoltaics. Exciton diffusion studies require accurate experimental techniques. This paper addresses two important complications that can arise in exciton diffusion length measurements made by analyzing luminescence from thin films on quenching substrates: namely, the effects of optical interference and of energy transfer to the quencher. When there is modest contrast in the refractive indices of the quencher and organic material, as is the case for titania or C_{60} and most organic materials, interference effects can overwhelm the measurement, thereby making it impossible to accurately determine the diffusion length of excitons in the organic material. We show that this problem can be fully eliminated by using thin (<5 nm) quencher films. The second complication that can occur is energy transfer to the quenching layer. We model the effect this has when fullerenes are used as quenchers. If energy transfer was ignored, one would falsely measure exciton diffusion lengths that are much greater than, and in some cases more than double, the actual diffusion length. Using titania as a quencher we eliminate the possibility of energy transfer, and by using thin titania films we eliminate the effects of interference and accurately measure a diffusion length of 6 ± 1 nm for the commonly used polymer poly[2-methoxy,5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2226687]

INTRODUCTION

Organic and hybrid inorganic/organic photovoltaics are under intense study and development because of their promise as low-cost solutions for the world's energy needs.[1–3] Efficiencies under simulated solar light of 5% or more have been reached recently[4,5] and are expected to continue to increase.[1,2] Many believe that device efficiencies must exceed 10% to enter the market as a viable source of energy.[6] To achieve such efficiencies, great effort has been under way to understand the photophysics and device physics of these promising technologies. While much is known about charge transport,[7–9] optical engineering,[10,11] and charge and potential profiles[12,13] in many architectures, very little is known about what factors limit the exciton diffusion length (L_D) in the organic semiconductors used. Future studies will hopefully lead to our understanding of what limits exciton transport and lead the way to design materials with larger L_D's. Key to these studies will be the ability to accurately and reproducibly measure L_D. A straightforward approach is to perform steady-state photoluminescence quenching experiments either in blends by tracking the luminescence intensity of the organic material as a function of added molecular quencher concentration or, as we prefer, by using a planar heterostructure geometry and monitoring luminescence intensity as a function of organic layer thickness. This latter measurement involves a comparison between the luminescence intensity of the organic material of interest on a quenching substrate and the intensity on a nonquenching substrate such as glass. By repeating this comparison for a range of film thicknesses, a model can be fitted to the data and an exciton diffusion length extracted. Important considerations for an accurate measurement are having flat and well-defined interfaces,[11,14,15] accounting for optical interference effects,[16] and correctly identifying and modeling the quenching mechanism.[17] We report that ignoring optical interference effects gives misleading results when using quenching materials that have modest refractive index contrast with the organic material. This effect explains why the measured values of the exciton diffusion length vary from 7 nm all the way to 20 nm for poly[2-methoxy-5-(2′-ethylhexyloxy) para-phenylenevinylene] (MEH-PPV).[18,19] Even when optical interference effects are properly taken into account by modeling the local optical field intensity in the heterostructures, interference effects can play such a profound role that they dominate the measurement. In other words, the quenching of excitons becomes second order compared to the effects of interference. In addition to these effects, we explore the consequences of Förster energy transfer from the polymer to the quenching substrate. If ignored, this too can lead to a large overestimation of the diffusion length when energy transfer is efficient. We conclude with calculations of energy transfer to fullerenes and comment on previous studies that incorporated fullerene quenching layers and did not consider energy transfer. Using titania as a quenching substrate and taking these issues into account, we measure a diffusion length of 6 ± 1 nm for poly[2-methoxy,5-(3,7-dimethyloctyloxy)]-1,4-phenylenevinylene (MDMO-PPV).

[a)]Author to whom correspondence should be addressed; electronic mail: mmcgehee@stanford.edu

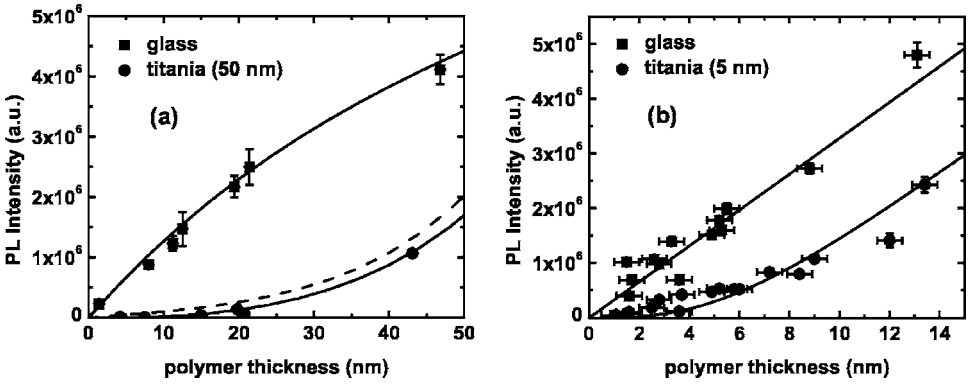

FIG. 1. Photoluminescence intensity vs MDMO-PPV thickness for the case of 50 nm titania (a) and 5 nm titania (b). The luminescence data for polymer on glass and titania are filled squares and circles, respectively. The model predictions in (a) are the numerical solutions to Eqs. (1) and (2) assuming $L_D=0$ nm (dashed) and $L_D=15$ nm (solid) and employing the optical properties of the materials used. The model predictions in (b) are given by Eq. (3) assuming $L_D=6$ nm.

EXPERIMENTAL DETAILS

Thin films of titania were used to quench excitons and were prepared using a sol-gel route as reported previously.[20] The thickness of the film was varied by controlling the titanium (IV) ethoxide concentration. The resultant precursor solution was spun on cleaned glass substrates at 2000 rpm. X-ray reflectivity and atomic force microscopy (AFM) showed both thicknesses of titania to have similar densities and surface morphologies. The polymer thickness was controlled by using a range of concentrations of polymer in chlorobenzene. All polymer films were spun on substrates at 2000 rpm in a nitrogen-filled glove box. The polymer thickness was measured using a combination of x-ray reflectivity, AFM, and absorption spectroscopy. The rms roughness of all interfaces was found to be less than 1 nm. Photoluminescence measurements were completed as previously reported,[21] but with the addition of a sealed chamber that holds the samples in nitrogen to protect them from photodegradation when they are removed from the glove box. Briefly, excitation was performed with *s*-polarized light from the 442 nm line of a HeCd laser, and the power density was kept below 10 $\mathrm{mW/cm^2}$.

RESULTS AND DISCUSSION

Interference effects

The photoluminescence data are shown as a function of MDMO-PPV film thickness for experiments incorporating 50 and 5 nm of titania quencher in Fig. 1 [(a) and (b) respectively]. In each case, the photoluminescence intensity of the polymer on glass monotonically increases with polymer thickness and does so linearly for thin films where the light is negligibly attenuated. Lower luminescence intensity is seen for the polymer films on both titania thicknesses. The major difference between the two data sets is the magnitude of reduction in luminescence intensity for the polymer film on titania. The luminescence of a 15 nm polymer film on 50 nm of titania is reduced by more than 90%, whereas the same thickness on a 5 nm titania film is reduced by less than 45%. Since the quenching of excitons by electron transfer should not depend on the quencher thickness, the roughness of both titania films are comparable, and quantum size effects should not be important as the film thickness of the titania is more than two times the reported Bohr exciton radius (<2 nm),[22] it is intuitive that the dependence of the luminescence intensity on titania thickness is likely due to interference effects.

Model

To model the experiment we solve the continuity equation for exciton density:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} + G(x), \tag{1}$$

where n is the exciton density, D is the exciton diffusion coefficient, τ is the natural exciton lifetime, and $G(x)$ is the rate at which excitons are generated as a function of position. At steady state this equation can be solved, given the boundary conditions for the two organic interfaces. We assume (1) $n|_{\mathrm{quench}}=0$ and (2) $-D(\partial n/\partial x)|_{\mathrm{nonquenching}}=0$ for the quenching and nonquenching interfaces, respectively. The first boundary condition is equivalent to saying that all excitons arriving at the interface are efficiently split. This assumption has been challenged before.[17,23] While ultrafast electron transfer from organic to titania has been reported,[24] we believe that this assumption may not entirely be true for some polymer/titania combinations.[25] It is difficult to exclude the possibility of imperfect quenching; however, we feel that the main conclusions of this paper are not based on this assumption. The second boundary condition simply states that there is no flux across a nonquenching interface. Using the appropriate boundary conditions, we solve for the exciton density distribution $n(x,d)$ for a given film thickness d. The measured photoluminescence is related to this density by

$$\mathrm{PL}(d) \propto \int_0^d n(x,d)\varepsilon(x)dx, \tag{2}$$

where $\varepsilon(x)$ is the light extraction efficiency.

Following others[11,16,26] we model the generation profile using a transfer matrix approach. However, we will later show that under certain circumstances the generation and emission efficiency profiles can be approximately constant and identical on both quenching and nonquenching substrates. In this case, there is a simple analytic solution for the photoluminescence as a function of film thickness:

$$\mathrm{PL}_{\mathrm{nonquench}}(d) = \gamma I_0 d,$$

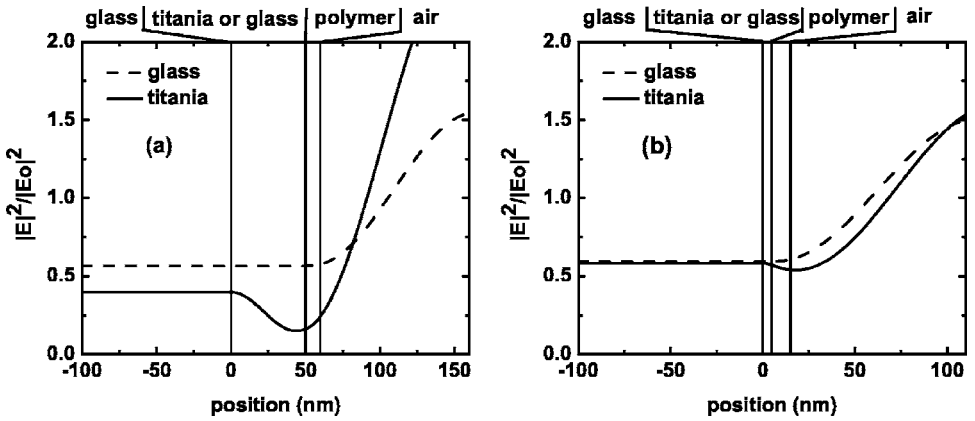

FIG. 2. Optical field intensity for excitation at 442 nm as a function of position in the heterostructures with 50 nm of titania (a) and 5 nm of titania (b). The intensities for the polymer on glass and titania are the dashed and solid lines, respectively.

$$\mathrm{PL}_{\mathrm{quench}}(d) = \gamma I_0 \left[d - L_d \tanh\left(\frac{d}{L_d}\right) \right], \tag{3}$$

where $L_D = \sqrt{D\tau}$ is the exciton diffusion length and γ is a proportionality constant. In this case when $d = L_D$, just over 3/4 of the excitons are quenched.

A numerical model is used for the predictions for 50 nm titania in Fig. 1(a), whereas the model predictions for 5 nm titania in Fig. 1(b) are from the above simple analytical solution. The 50 nm titania data appear to fit a model assuming a 15 nm diffusion length, whereas the 5 nm titania data fit a model assuming a diffusion length of only 6 nm. This difference can easily be explained by considering the effects of interference.

At the excitation wavelength, titania has a refractive index of $n_{\mathrm{titania}} = 2.53$, whereas glass and polymer have refractive indices of $n_{\mathrm{glass}} = 1.53$ and $n_{\mathrm{polymer}} = 1.3 + 0.35i$, respectively.[27,28] Thus we can expect strong reflections at the polymer/titania and titania/glass interfaces. Figure 2 shows the optical field intensity for excitation at 442 nm, which is proportional to the exciton generation rate, as a function of position in each of the heterostructures incorporating both 50 and 5 nm films of titania for a 10 nm polymer film. For comparison, the profile is also shown in each graph for the case where titania is absent. Considering the 50 nm titania case first, there is 60% less exciton generation when the polymer is on the titania compared to the polymer on glass. Furthermore, the greatest disparity occurs near the quenching interface. Simply put, fewer excitons are generated near the interface of the polymer and titania. Similar calculations for the emission show that the emission efficiency is also depressed near the polymer/titania interface. These two compounding effects lead to nearly all the observed reduction in photoluminescence intensity for the polymer on titania relative to the polymer on glass. Two model predictions are shown in Fig. 1(a). The dashed line is generated assuming $L_D = 0$ nm, whereas the solid line as mentioned is generated assuming $L_D = 15$ nm. Since there is no diffusion and subsequent quenching, the dashed line shows the reduced intensity which arises solely from interference effects. The additional reduction in luminescence intensity due to exciton diffusion and subsequent quenching given by the solid line is clearly a secondary effect. We conclude that using 50 nm titania films as the quencher makes it impossible to accurately determine the diffusion length for $L_D < \sim 20$ nm.

Figure 2(b) shows the case for a 5 nm titania film. For the same 10 nm polymer film there is a less than 8% reduction in the field intensity when titania is present, which is within our experimental error. Furthermore, in contrast to the former case, a small difference in field intensity occurs at the polymer/titania interface, and the field intensity is fairly constant throughout the polymer layer. Modeling shows that using a 5 nm titania layer or less allows us to treat the generation rate as constant for thin polymer films ($< \sim 15$ nm) and to use the same generation rate for the same polymer thicknesses on quenching and nonquenching substrates. This is an important point that also applies to other quenchers, such as fullerenes, with refractive indices larger than the polymers' at the pump and emission wavelengths. When the diffusion length is small (<10 nm), interference effects can be avoided by using thin quencher films and polymer films less than ~ 20 nm. However, when the diffusion length and polymer film thicknesses are larger, the generation profile cannot be assumed to be constant and must be numerically modeled.

Effects of energy transfer to the quencher

Most exciton diffusion length measurements assume that the only quenching mechanism is the splitting of the exciton by electron transfer at the organic material/quencher interface. While this is certainly true for wide band gap quenchers such as titania, it is not necessarily true for others. When the quencher has a lower band gap than the polymer and the joint density of states is appreciable, Förster energy transfer can also quench excitons by nonradiative transfer of the exciton from the organic material to the quencher. The rate of Förster transfer is

$$k_F(r) = \frac{1}{\tau}\left(\frac{R_0}{r}\right)^6 \tag{4}$$

for two point dipoles[29] separated by a distance r, where R_0 is the Förster radius and is typically 1–4 nm. Since R_0 is often less than L_D, many believe that this leads to a negligible enhancement of exciton harvesting. However, the enhancement can be appreciable in a planar heterostructure where the exciton can be transferred to any quencher molecule in the quenching film.[21] In this case the rate of energy transfer goes as $1/x^4$ for a monolayer[30] of quencher and $1/x^3$ for thick quenching films,[31] where x is the distance from the exciton to the organic material/quencher interface.

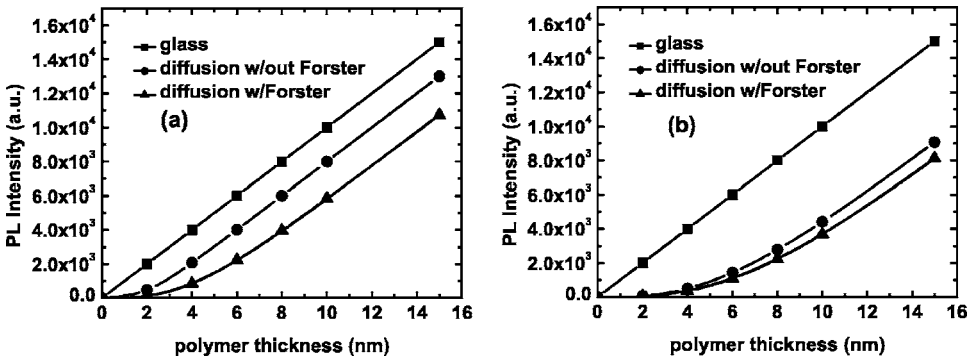

FIG. 3. Predicted photoluminescence vs organic thickness with and without energy transfer (Förster radius of 2 nm) for L_D=2 nm (a) and L_D=6 nm (b). The luminescence intensities of the organic material without quenching, with diffusion but no energy transfer, and with both diffusion and energy transfer are shown as the lines with filled squares, circles, and triangles, respectively. A model incorporating only diffusion with an effective diffusion length was fitted to the predicted data for the case where energy transfer is present. These model lines cannot be seen as they so closely fit the model predictions incorporating energy transfer. These fits yield effective diffusion lengths of 4.3 and 7.1 nm which are found for the 2 and 6 nm data, respectively.

To model the enhancement of exciton harvesting, we solve a modified exciton continuity equation:

$$\frac{\partial n}{\partial t} = D\frac{\partial^2 n}{\partial x^2} - \frac{n}{\tau} - k_F n + G(x), \tag{5}$$

where k_F is the spatially dependent energy transfer rate given by

$$k_F(x) = \frac{C_A}{\tau}\frac{\pi}{6}\frac{R_0^6}{x^3}, \tag{6}$$

where C_A is the energy acceptor molecular density and R_0 is the Förster radius.

Of particular interest is the possible effect of energy transfer when fullerenes are used as quenchers. We have previously shown that Förster transfer can occur between organic chromophores and the derivatized fullerene [(6,6)-phenyl C_{61} butyric acid methyl ester] (PCBM).[32] Because fullerenes are often used as quenchers in diffusion length measurements, it is important to quantify the possible enhancement in luminescence quenching from energy transfer in these experiments. Using the absorption spectrum of PCBM and the emission spectrum of MDMO-PPV and assuming randomly oriented chromophores and an emission quantum efficiency of 0.2, we calculate R_0 to be $\sim$2 nm.[29] Using the density of C_{60},[33] 1.7 g/cm^3, we calculate an acceptor density of $\sim$1.4/nm^3. The predicted photoluminescence versus polymer thickness with and without energy transfer can be calculated using these parameters. Figure 3 shows the model predictions for cases where L_D equals 2 nm [Fig. 3(a)] and 6 nm [Fig. 3(b)]. Fits, for the cases when energy transfer is present, yield an "effective diffusion length." This is the diffusion length that would be extracted from an experiment where quenching is due to both exciton diffusion and energy transfer. Intuitively, we would expect a larger enhancement in exciton harvesting for smaller diffusion lengths. For the 2 nm "actual" diffusion length, the enhanced quenching from energy transfer leads to an effective diffusion length of 4.3 nm. In other words, if energy transfer was not considered, one would mistakenly interpret the quenching data as arising from a diffusion length of 4.3 nm when, in fact, the majority of the quenching would have come from energy transfer. As expected the enhancement is less dramatic for a polymer with a 6 nm diffusion length [Fig. 3(b)]. In this case the enhanced quenching from energy transfer leads to an effective diffusion length of 7.1 nm. Markov *et al.* recently reported diffusion length measurements on a series of PPV derivatives using a polymerized fullerene as a quencher.[18] They found that materials of varying energetic disorder have similar diffusion lengths. While they postulated that there existed a constant exciton trap density to explain their data, perhaps energy transfer to the fullerene quencher may contribute to the lack of variation in their measured diffusion lengths.

It is insightful to quantify the fraction of excitons that undergo energy transfer versus electron transfer. This is easily done by considering the exciton density distribution. Fick's first law determines the flux of excitons at any point in the organic material, given the exciton distribution. By considering the flux of excitons across the quenching interface we can determine the fraction of excitons that undergo charge transfer. Comparing this value to the total fraction of quenched excitons then gives the fraction that undergoes energy transfer. Figure 4 shows the exciton density as a function of position for a 10 nm organic film with a uniform generation rate, for both 2 nm [Fig. 4(a)] and 6 nm [Fig. 4(b)] L_D. There are two important aspects to mention in these plots. The first is that the total number of excitons is lower when energy transfer is present because of the enhanced exciton harvesting. The second is that the spatial derivative of the exciton density at the quenching interface is lower when energy transfer is present. This necessarily implies that the number of excitons undergoing charge transfer is smaller when energy transfer can occur. For the 2 nm diffusion length when energy transfer is present, 42% of the excitons are quenched (up from 20% for diffusion and only electron transfer). Of these about half are quenched via energy transfer and half via electron transfer. For the 6 nm diffusion length, there is a small enhancement in exciton quenching (63% up from 56%). In spite of the small enhancement, the number of excitons undergoing electron transfer is still reduced by about one-third when energy transfer is present. One practical implication of this reduction is that to extract

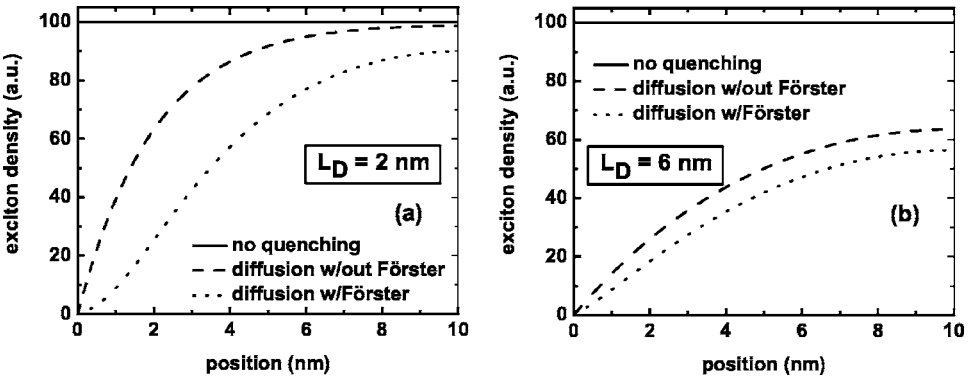

FIG. 4. Exciton density as a function of position in a 10 nm polymer film for 2 nm (a) and 6 nm (b) diffusion lengths. The quenching interface is at 0 nm, and the radius of C_{60} (~0.5 nm) is used to properly account for the nonzero size of the C_{60} molecules. The solid line shows the exciton density in the case where quenching is absent, whereas the dashed and dotted lines show the respective densities when quenching without and with energy transfer is present.

all charges corresponding to quenched excitons in a photovoltaic device, there must be efficient hole transfer from the quencher to the organic material for any excitons that undergo energy transfer. Consequently, the offset in donor-acceptor highest occupied molecular orbital (HOMO) levels is an important parameter to optimize.

CONCLUSIONS

We have explained how optical interference effects and energy transfer to the quencher can affect exciton diffusion length measurements using luminescence quenching. When there is modest contrast in the refractive indices of the organic material and quencher, as is the case for titania or C_{60} and most organic materials, interference effects can overwhelm the measurement, thereby making it impossible to accurately determine the diffusion length of excitons in the organic material. We showed that this problem can be fully eliminated by using thin (<5 nm) quencher films. The second complication that can arise involves the nature of the exciton quenching mechanism. We showed to what extent Förster transfer can enhance exciton harvesting when fullerenes are used as quenchers. If this was ignored, one would falsely measure diffusion lengths of 4.3 and 7 nm for materials with actual diffusion lengths of 2 and 6 nm, respectively. Using titania as a quencher, we eliminate the possibility of energy transfer. And by using thin titania films, we eliminate the effects of interference and accurately measure a diffusion length of 6 ± 1 nm for MDMO-PPV.

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