PHYSICAL REVIEW B **82**, 205211 (2010)

Diffusion length of triplet excitons in organic semiconductors

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(Received 22 April 2010; revised manuscript received 17 September 2010; published 23 November 2010)

The exciton diffusion length in organic semiconductors strongly impacts the efficiency of energy harvesting organic optoelectronics. We demonstrate an experimental technique to estimate the diffusion length of triplet excitons in a ladder-type conjugated organic semiconductor from quenching of the triplet-triplet absorption in the presence of acceptor molecules. The diffusion lengths are consistent with a phenomenological random-walk model. Experiments on two different molecular weights of the polymer sample show that the diffusion length of triplet excitons is in the few micrometers range and depends upon the size of the π-conjugated system.

DOI: 10.1103/PhysRevB.82.205211 PACS number(s): 78.66.Qn, 78.47.−p, 71.35.Cc

I. INTRODUCTION

The application of semiconducting conjugated polymers (CPs) in organic photovoltaics (OPVs) (Ref. 1) and light-emitting diodes (OLEDs) (Ref. 2) depends critically on the formation, transport, recombination, and separation of excitons. In OLEDs, the injection of charges in the organic material leads to the formation of triplet and singlet excitons, which are then harvested to produce light. Although most of the bulk heterojunction OPVs use light to excite molecules into singlet excitons, the short lifetime of singlets limits their migration to interfaces for dissociation. Recently, it was found that, when trace amounts of a heavy metal, such as Pd, is incorporated into the backbone of an organic polymer, it opens up a route for harvesting triplet excitons.[3] The presence of triplet states further enhances solar cell efficiency over singlet-state-only cells.[4,5]

Despite considerable progress in device construction, an understanding of the basic processes remains elusive due to the immense complexities of the systems involved. Clearly, a better knowledge of the fundamental processes would be helpful for an optimization of the aforementioned devices. However, experiments on the dynamics of triplets are lacking primarily due to the difficulties associated with direct optical studies of triplet states since singlet-triplet transitions are forbidden. For instance, the time-resolved spectroscopic techniques of thickness-dependent quenching of excitons,[6–10]which have been quite successful in determining exciton diffusion length (L) and diffusivity (D) of singlet excitons, are not available for triplet excitons. Only recently, the use of organometallic polymers and improvements in spectroscopic techniques have made it possible to explore fundamental properties of triplet excitons.[11] Nevertheless, the values obtained for some of these properties have been inconsistent due to the differences in techniques, sample preparations, and methods of analysis.

The diffusivity of triplet excitons in organic semiconductor thin films of diaryl (diphenyl)-substituted ladder-type poly(paraphenylene) (PhLPPP) containing a trace concentration of covalently bound Pd atoms was found to be $20 \pm 1 \times 10^{-6}$ cm^2/s,[12] while for a polycrystalline film of a platinum(II) porphyrine complex, PtOEP, the diffusivity was 4×10^{-6} cm^2/s and 6.2×10^{-8} cm^2/s for the monomer and dimer triplets, respectively.[13] Furthermore, the diffusivity in organic crystals such as anthracene is 2×10^{-4} cm^2/s.[14] Additionally, the reported lifetimes of triplet excitons in organic materials span a wide range from a few microseconds[13] to a few milliseconds.[15] This translates into a large range for exciton diffusion lengths from a few nanometers to a few micrometers. Hence, a reliable method of determining triplet exciton diffusion lengths, especially in triplet-enhanced CPs, is necessary for their application in OPVs.

Time-resolved phosphorescence quenching has been typically used to measure the triplet exciton diffusion lengths.[3,12] However, this technique is valid only for phosphorescent CPs and not a general method since many CPs do not show phosphorescence, even though a small amount of triplet states is typically generated under optical excitation due to the intersystem crossing (ISC).

Here, we propose a method for determining the triplet exciton diffusion length utilizing photoinduced absorption (PIA) spectroscopy. Our method is based on the quenching of the triplet-triplet (T-T) absorption by acceptor molecules, where the intensity of the T-T absorption depends on the concentration of the acceptor molecules. The method is more generally applicable since it relies only on ISC and not on the phosphorescence. We further show that a phenomenological quasi-one-dimensional (1D) random walk with absorbing wall models the diffusion process well and could be used to deduce diffusion length from the diffusivity of the random walker and the triplet exciton lifetime.

The paper is organized as follows: the experimental details are presented in Sec. II, the results of the PIA experiments are discussed in Sec. III, the theoretical model is described in Sec. IV followed by a discussion in Sec. V. Finally, in Sec. VI, we summarize our results.

II. EXPERIMENTAL DETAILS

A. Sample preparation

We illustrate our method for triplet diffusion length by the quenching of T-T absorption in two different PhLPPP polymer samples,[16] a high molecular weight (M_n=14 700 g/m)

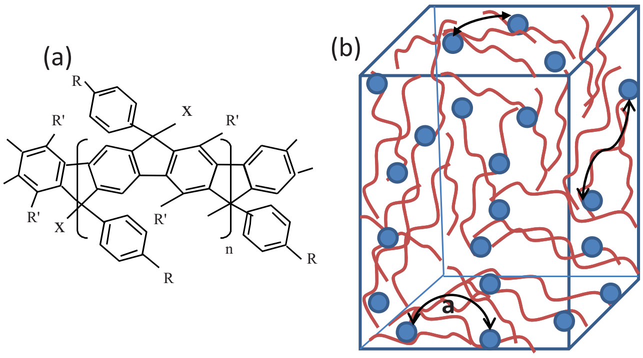

FIG. 1. (Color online) (a) Chemical structure of PhLPPP. R and R' refer to $C_{10}H_{21}$ and C_6H_{13}, respectively, and X is a phenyl group. (b) Illustration of a quasi-one-dimensional model of exciton diffusion through the polymer chains in a 3D space. Here a is the average distance between PCBM molecules, shown by blue circles, along the path of diffusion.

(PhLPPP-H) with polydispersity of 1.3 and a low molecular weight (M_n=3800 g/m) (PhLPPP-L) of polydispersity ~1.6, by an electron acceptor, [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM), which was purchased from Sigma-Aldrich Co. Figure 1(a) shows the chemical structure of PhLPPP. The main advantage of using PhLPPP is that the experiments could be performed at room temperature (RT) since a trace amount of Pd in the PhLPPP backbone results in a high fraction of triplet excitons at RT.[3] PhLPPP:PCBM blends were prepared in various molecular ratios, from 50:1 to 10 000:1 by dissolving the components in dichlorobenzene. Equal volumes of various blends were carefully drop-cast onto glass substrates so that the final dried sample areas were same for all blends as determined by visual inspection. No phase separation in the mixture was observed for low concentrations of PCBM as verified by an atomic force microscope.

B. Methodology

The PIA spectra were measured using the 325 nm line of a HeCd laser as the pump beam, modulated by a mechanical chopper. A 100 W quartz tungsten halogen lamp was used to probe the beam, and a silicon detector was used to detect the transmitted light. The small changes (ΔT) in transmission were obtained by passing the signal from the detector to a preamplifier and then to a lock-in amplifier (SR810) referenced to the chopper frequency. All photomodulation spectra are given by $-\Delta T$ divided by the transmission (T). For the lifetime measurements the R channel of the lock-in, which is the vector magnitude of the dual phase, was used since we are interested only in the amplitude of the periodic signal and not its phase.

III. PIA RESULTS

A. Estimating diffusion length from triplet-triplet quenching

The T-T absorption peak appears at 963 nm and 940 nm for PhLPPP-H and PhLPPP-L, respectively. The inset of Fig. 2 shows the quenching of the T-T absorption for PhLPPP-H as the PhLPPP:PCBM molar ratio decreases. A similar behavior is seen for PhLPPP-L. Since the average distances between PCBM molecules are much larger than singlet exciton diffusion lengths,[17] we attribute the quenching of the PIA signal to the loss of triplet energy to the PCBM molecules situated along the polymer chain. The triplet excitons of PhLPPP migrate along the polymer chain and hop from one chain to another until they encounter a PCBM molecule, as schematically shown in Fig. 1(b). Thus, although PCBM molecules are distributed in a three-dimensional (3D) space, an exciton migrates from the location of generation to the PCBM from chain to chain in a quasi-one-dimensional path. We determine the average separation of the PCBM molecules along a sequence of polymer chains from the product of the molar ratio, R, and the length of a single polymer chain. Assuming that the average length of a one-dimensional conjugated π system in PhLPPP is l_p, and there are N_{PhLPPP} molecules per N_{PCBM} molecules, then the average distance between the PCBM molecules that the exciton may diffuse is given by

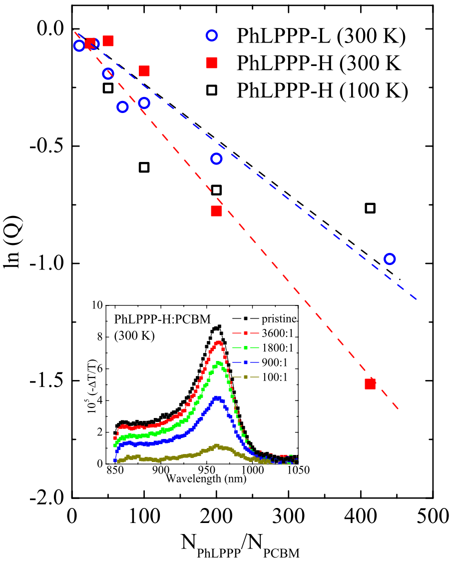

FIG. 2. (Color online) Logarithm of the quenching factor Q versus PhLPPP:PCBM molar ratio for PhLPPP-L [open (blue) circles] and PhLPPP [filled (red) squares] at 300 K. The open (black) squares are the quenching data of PhLPPP-H at 100 K. The dashed lines are linear fits to the data. The inset on the bottom shows the quenching of the PIA signal from PhLPPP-H for selected values of PhLPPP:PCBM ratio at 300 K.

$$a = \left(\frac{N_{\text{PhLPPP}}}{N_{\text{PCBM}}} \right) l_p \equiv R l_p. \tag{1}$$

Further, for a unimolecular quenching we expect the T-T absorption peak, as determined by $-\Delta T/T$, to depend exponentially on a, or equivalently on R, as follows:

$$\frac{\Delta T}{T} = \left(\frac{\Delta T}{T} \right)_0 [1 - e^{-Rl_p/L}], \tag{2}$$

where $(\Delta T/T)_0$ is the PIA signal for the pristine sample as $R \rightarrow \infty$, and L is the diffusion length. We find it more convenient for the discussion to introduce a quenching factor Q by the following relation:

$$Q \equiv 1 - \frac{\Delta T/T}{(\Delta T/T)_0}. \tag{3}$$

Equation (2) can be reorganized so that a plot of the signal versus R is expected to be a linear function, as shown in Fig. 2, whose slope is related to the diffusion length by

$$\ln(Q) = -Rl_p/L. \tag{4}$$

Arguably, if the diffusion is not one dimensional, Eq. (1) could be written as $a=R^{1/n}l_p$, where n is the spatial dimension with a value between 1 and 3. For a strictly 1D diffusion, $n=1$. We compare the diffusivity of triplet excitons estimated by our method with $n=1$ to that obtained by Reufer *et al.*[12] for PhLPPP using a different technique. The two values are very close to each other, further justifying the usage of Eq. (1) with $n=1$. In Sec. V we discuss the validity of the quasi-one-dimensional diffusion in detail.

We point out that Q is independent of the chopper frequency since it depends on the ratio of the T-T signal of the blend to that of the pristine sample. The amplitudes of the T-T peak change proportionately for the blended and the pristine sample upon changing the chopper frequency. From the slope of the quenching graph in Fig. 2, we can find L by calculating its inverse and multiplying the result by the appropriate l_p of the polymer, which is approximately 4 nm and 14 nm for PhLPPP-L and PhLPPP-H, respectively, obtained from the chemical structures of the oligomers and bond lengths. At 300 K, the slopes for PhLPPP-L and PhLPPP-H in Fig. 2 are -0.0024 ± 0.0002 and -0.0036 ± 0.0002, respectively. Thus, the data given in Fig. 2 give the diffusion lengths for triplet excitons in PhLPPP-L and PhLPPP-H as 1.7 ± 0.2 μm and 3.9 ± 0.3 μm, respectively. Quenching of the PIA was further carried out at 100 K for PhLPPP-H. From the slope in Fig. 2 the diffusion length was estimated as 6.0 ± 0.6 μm at 100 K.

B. Triplet lifetimes and diffusivity in PhLPPP

We further determine the diffusivity of triplet excitons using the following relation:

$$D = L^2/\tau, \tag{5}$$

where τ is the triplet lifetime. To determine the lifetime of the triplet exciton, we note that in our PIA experiments, the excitation of the molecules from the ground state, S_0, to the singlet excited state, S_1, is achieved by a periodic modulation of the exciting laser beam at the chopper frequency. Assuming that, at low concentrations of PCBM, the triplet lifetime is dominated by a monomolecular decay of the triplets to the ground state, it can be shown that the triplet population (T_1) generated by ISC from S_1 to T_1 with the chopper frequency (f) as

$$|T_1| = \frac{C}{\sqrt{1+(2\pi f\tau)^2}}, \tag{6}$$

where C is a constant.[18,19] Since the PIA signal is proportional to the triplet population and we are interested only in the amplitude of the periodic signal we use the R channel of the lock-in amplifier, vary chopper frequency f, and fit the resulting curve according to Eq. (6) as shown in Fig. 3. The lifetime of the triplet excitons depends both on the chain length of PhLPPP and the PCBM concentration. The inset of Fig. 3 shows the variation in τ as a function of the PCBM concentration, where the asymptotic values as $(N_{\mathrm{PhLPPP}}/N_{\mathrm{PCBM}}) \to \infty$ correspond to the lifetimes of the pristine samples, which are found to be 17.0 ± 0.5 ms and 11.0 ± 0.3 ms for PhLPPP-L and PhLPPP-H, respectively. This trend is consistent with the observations in oligo(p-phenylene vinylene)s, where shorter oligomers have longer triplet lifetimes compared to the longer oligomers.[20] The standard deviations are obtained by fitting the experimental data in Fig. 3 to Eq. (6). τ was also measured for PhLPPP-H at 100 K, and was found to be 12.0 ± 0.2 ms.

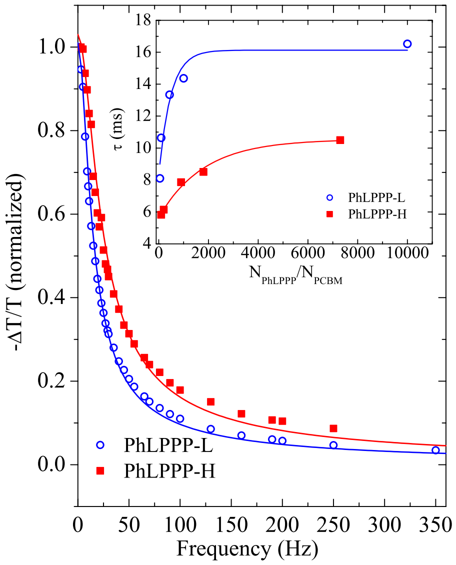

FIG. 3. (Color online) The peak PIA signals for T-T transition in PhLPPP-L and PhLPPP-H as a function of the chopper frequency at 300 K. The data are fit to Eq. (6) to obtain triplet lifetimes (τ). The variation in τ with PhLPPP:PCBM ratio is shown in the inset, which reaches 17 ms and 11 ms asymptotically, the lifetimes for pristine PhLPPP-L and PhLPPP-H samples, respectively.

The triplet diffusivities calculated from the diffusion lengths and lifetimes of the pristine samples at 300 K using Eq. (5) are listed in Table I. The diffusivities of the triplet excitons in PhLPPP-L and PhLPPP-H are found to be $(1.7 \pm 0.2) \times 10^{-6}$ cm^2/s and $(1.4 \pm 0.1) \times 10^{-5}$ cm^2/s, re-

TABLE I. Various PhLPPP triplet exciton properties at 300 K: experimental and theoretical diffusion lengths L and L_{th}, lifetime τ, and experimental and theoretical diffusivities D and D_{th}.

	PhLPPP-L	PhLPPP-H
L	1.7 ± 0.2 μm	3.9 ± 0.3 μm
τ	17.0 ± 0.5 ms	11.0 ± 0.3 ms
D	$(1.7 \pm 0.2) \times 10^{-6}$ cm^2/s	$(1.4 \pm 0.1) \times 10^{-5}$ cm^2/s
D_{th}	8.0×10^{-7} cm^2/s	8.0×10^{-6} cm^2/s
L_{th}	1.2 μm	3.0 μm

spectively at 300 K, which are consistent with the expectation that excitons would be more readily diffusible in a longer chain molecule than a shorter one, and hence, would have a larger diffusivity. In our experiments the diffusivity of PhLPPP-H at 100 K was found to be $(3.0\pm0.2)\times10^{-5}$ cm^2/s. Reufer *et al.*[12] observed a temperature-independent diffusion for triplet excitons below 200 K in a high molecular weight PhLPPP sample using phosphorescence decay experiments, with average value of $D \sim 2.0\pm0.1\times10^{-5}$ cm^2/s. The value of D obtained here compares well with the values given in Ref. 12, the difference being attributable to the difference in molecular weights of the sample used in the two studies, which further supports the quasi-1D model used in this work to obtain the diffusion length.

The diffusivities obtained here for the two samples of PhLPPP are in agreement with the diffusivities of triplet excitons in other systems.[13] Our diffusion lengths differ from the values of Pt(II) porphyrine complexes in Ref. 13, which may be attributed to the large difference in triplet lifetimes in the two systems; while triplets in PhLPPP have lifetimes on the order of tens of millisecond, the reported triplet lifetimes in PtOEP have values in the microseconds.

IV. RANDOM-WALK DIFFUSION OF EXCITONS

A. Model

Our experimental data are further modeled by a one-dimensional random walk since the average distance that an exciton travels on a polymer chain is typically longer than it covers in hopping between chains, unlike in a molecular crystal.[21,22] We consider the diffusion of the triplet excitons to occur as random hops of step size d and the hopping time τ_0, which depend on the overlap of molecular orbitals between the two sites involved. Further, we assume that the molecules are sufficiently close together for the intermolecular hopping distances and times to be not significantly different from d and τ_0. In order to capture the exciton dynamics, we require that the exciton hopping time be much less than the exciton lifetime, i.e., $\tau_0 \ll \tau$, and monomer-monomer distance be less than the distance a between two PCBM molecules, i.e., $d \ll a$.

B. Estimating diffusion length using a random-walk model

Casting the problem at hand as a random-walk problem with an absorbing wall,[23] at the average PCBM distance from the front of the sample as shown in the inset of Fig. 4, we arrive at the following for the fraction of the excitons generated at $x=0$ that arrive at $x=a$ during time t and $t+dt$ as:

$$q(a,D_{th},t)dt = \frac{a}{2\sqrt{\pi D_{th}}} e^{-a^2/4D_{th}t}dt, \tag{7}$$

where D_{th} is the diffusion constant in the theoretical model. Therefore, if the steady-state population of triplets in the absence of PCBM is P_0, then the population in the presence of PCBM is

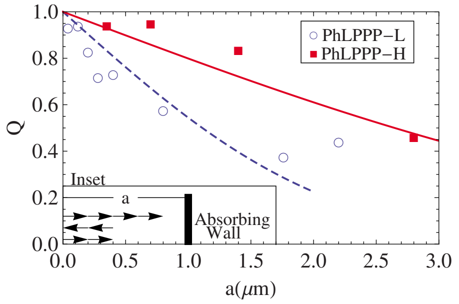

FIG. 4. (Color online) Quenching of T-T transition modeled by a random-walk with an absorbing wall. The open (blue) circles and the filled (red) squares are the experimental data for the normalized quenching of the T-T transition at 300 K in PhLPPP-L and PhLPPP-H, respectively. The dashed (blue) and the solid (red) lines are $Q_{th}(D_{th},a)$. The inset shows a schematic of the random-walk model.

$$P = P_0\left[1 - \int_0^{\tau} q(a,t)dt\right]. \tag{8}$$

Since the T-T absorption is proportional to the steady-state population of triplets, the PIA signal decreases with increasing PCBM concentration according to Eq. (8). Clearly, the decrease in T-T absorption is not linear in the concentration of PCBM as would be expected if there were no exciton migration contribution.[24] The PIA signal of a PhLPPP:PCBM mixture normalized with the PIA signal of the pristine PhLPPP can be written in terms of the theoretical quenching factor Q_{th} which is a function of a and D_{th},

$$Q_{th}(D_{th},a) = 1 - \frac{P}{P_0} = \int_0^{\tau} q(a,D_{th},t)dt, \tag{9}$$

where the subscript 0 refers to the pristine PhLPPP sample. To deduce the triplet diffusivity based on Eqs. (7)–(9), we fit the quenching of PIA data by the theoretical quenching Q_{th} given in Eq. (9) as shown in Fig. 4. The best fit of the data was obtained for $D_{th}=8\times10^{-7}$ cm^2/s and $D_{th}=8\times10^{-6}$ cm^2/s for PhLPPP-L and PhLPPP-H, respectively. The theoretical diffusivities are comparable to the experimental values, which lends support to the random-walk diffusion model proposed here for the diffusion of triplet excitons in ladder-type polymers. In order to obtain the diffusion length (L_{th}) using the random-walk model, we use Eq. (5) with the above D_{th} and the experimental lifetime τ. The triplet exciton diffusion lengths obtained in this way are 1.2 μm and 3.0 μm for PhLPPP-L and PhLPPP-H, respectively, consistent with the experimental values.

V. DISCUSSION

The diffusivity of triplet excitons in PhLPPP determined by our experiment ranges between 10^{-5}–10^{-6} cm^2/s. This is close to the diffusivity of triplet excitons reported in a variety of conjugated systems in the literature.[13,25] The ∼ μm range diffusion length stems from long lifetimes of the triplet excitons in the system under investigation. We have determined the diffusion length/diffusivity of triplet excitons by two methods: directly from the amount of quenching of the T-T absorption in PIA experiment as a function of PCBM concentration, and the other by solving the problem as a random-walk model using some experimental input. In both cases the separation of PCBM molecules (a) is evaluated using a quasi-1D diffusion path. Since the experiments are from blended film samples, there is some amount of nonuniformity and additionally, there may be variations as to which area of the film was illuminated. Despite these variations we point out that our value for D (at 100 K) $\sim 3\times 10^{-5}$ cm^2/s in PhLPPP-H is very close to the value (2×10^{-5} cm^2/s) measured in Ref. 12 by an alternate method without the use of any acceptor molecules. The agreement between the values of diffusivity of triplet excitons found by two different methods further lends support to the method presented here.

The effective dimension for the diffusion of excitons can be ascertained if we assume that the total volume of the sample may be written as either $N_{\mathrm{PCBM}}a^n$ or $N_{\mathrm{PhLPPP}}b^n$, where a is the separation between PCBM molecules, b the distance between centers of the PhLPPP polymer chains, and n the spatial dimension. Here b would be proportional to the π-conjugation length l_p of a PhLPPP polymer chain, i.e., $b=cl_p$, where the proportionality constant $c=1$ for a tightly packed polymer matrix and $c>1$ for a sparsely packed system. Assuming a tightly packed structure in the present system, we note that the separation between PCBM molecules may be given as $a=R^{1/n}l_p$, where R stands for the molar ratio $N_{\mathrm{PhLPPP}}:N_{\mathrm{PCBM}}$ as mentioned above in Sec. III A. Using this expression for a in Eq. (2) in place of $a=Rl_p$, the value of n could be deduced from the quenching data given in Fig. 2. We find that $n\approx 1$ for PhLPPP-H and $n\approx 1.3$ for PhLPPP-L. These values of spatial dimensions in which the excitons migrate are very near 1, and show that the one-dimensional model is appropriate for the analysis in the present system. Furthermore, for the low molecular weight sample, since n is not strictly 1, our procedure overestimates the diffusion length. Clearly, diffusion in molecular samples, where the diffusion is more likely three dimensional, one would need a three-dimensional random-walk model to analyze the results. Note that, in the formula for a, the factor c multiplies l_p, which essentially extends the distance an exciton travels between PCBM molecules. Therefore, if the system is not tightly packed, i.e., when $c>1$, then the same level of quenching would result in a larger value of the diffusion length, assuming dissipation of energy during hops is unaffected by an increase in the hopping distance. Furthermore, although, the theoretical one-dimensional model is strictly applicable to systems with large π-conjugation lengths compared to the hopping distance between molecules, the experimental procedure given here should be more generally applicable as long as we express the inter-PCBM distance a in terms of n and deduce n from experiment as outlined here. Even with an uncertainty in the value of c, the determination of the triplet exciton diffusion length could be achieved by the PIA quenching method which would be accurate within the margin of uncertainty of the factor by which distance between PhLPPP molecules differs from the π-conjugation length of the molecule.

In our studies, we have also assumed that PCBM molecules are very effective in quenching the triplet excitons, which is based on the observation that in a 1:1 molar ratio of PhLPPP:PCBM the PIA signal is completely quenched. Note that, if the efficiency of quenching by PCBM molecules were not 100%, then it would require multiple encounters with PCBM molecules for the energy in the exciton to dissipate. Thus, a lower efficiency of quenching would yield even larger value of the diffusion length. Since our results from quenching experiments agree well with those of Reufer *et al.*[12] using phosphorescence, we believe that the assumption of high quenching efficiency by PCBM molecules is justified in the final analysis. Further work in exploring the efficiency of quenching of excitonic energy in other donor/acceptor systems will be invaluable.

VI. SUMMARY

In summary, we present a simple experimental technique in conjunction with a random-walk model for determining triplet exciton diffusion lengths in organic semiconductors. This relies on the quenching of the T-T absorption in the presence of acceptor molecules. Since this method is based on the T-T absorption rather than phosphorescence, it may be applied to even nontriplet enhanced CP, with a caveat that the experiments may have to be performed at lower temperatures as the T-T absorption signal in general may be weak at RT. The use of a Pd-incorporated ladder-type polymer in this work facilitated the PIA measurements at RT. The triplet diffusion lengths determined in the ladder-type polymer, PhLPPP, depend on the length of the π-conjugated system and are in the 1–4 μm range at 300 K. The long diffusion lengths of the triplet excitons compared to singlet excitons, which are typically in the nanometer range, open up a new realm of application of triplet-enhanced CPs in energy harvesting optoelectronics.

ACKNOWLEDGMENTS

We acknowledge the support of this work through the University of Missouri Research Board and partial support from the National Science Foundation under Grant No. ECCS-0823563. M.S. acknowledges Truman State University for a sabbatical grant.

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