THE JOURNAL OF PHYSICAL CHEMISTRY C

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Probing Enhanced Exciton Diffusion in a Triplet-Sensitized Organic Photovoltaic Cell

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Cite This: J. Phys. Chem. C 2020, 124, 3489−3495 Read Online

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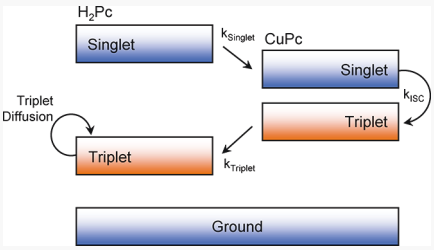
ABSTRACT: We examine exciton diffusion in a triplet-sensitized organic photovoltaic cell, where transport occurs via the long-lived triplet state of a fluorescent electron donor. While the triplet state is optically dark, it is populated via sensitization by a guest species capable of intersystem crossing. Here, the host material is metal-free phthalocyanine (H_2Pc), and the triplet-sensitizing guest is copper phthalocyanine (CuPc). Optical excitation of H_2Pc leads to the generation of singlet excitons which rapidly undergo energy transfer to CuPc. Excitons on CuPc undergo intersystem crossing to the triplet state followed by energy transfer back to the H_2Pc triplet state. The exciton diffusion length (L_D) is extracted using an internal quantum efficiency ratio methodology that permits accurate device-based measurements of exciton transport even in the presence of geminate recombination losses. The donor layer L_D varies with composition with a maximum L_D of (13.4 ± 1.6 nm) observed at 20 vol % CuPc, an almost 60% increase over the case of the mobile H_2Pc singlet. Despite this increase, further improvements may be possible as the neat-film H_2Pc triplet L_D is estimated to exceed (20.7 ± 5.0) nm.



INTRODUCTION

The design of organic photovoltaic cells (OPVs) is strongly dictated by the short exciton diffusion length (L_D) of the component active materials. Indeed, it is the short L_D that led to the development of the bulk heterojunction architecture to increase exciton harvesting.[1−10] Increased active material L_D is desirable as it could relax the spatial constraints on film morphology in bulk heterojunctions or permit the realization of efficient, planar heterojunction OPVs. Several works have previously examined the potential for increased L_D through the use of long-lived triplet excitons.[11−16] The challenge with the use of such states is their low optical absorption, making them less accessible under optical pumping.

Prior work has demonstrated the ability to overcome the challenge of low optical absorption through the use of a host−guest, triplet-sensitized OPV.[16−27] In a triplet-sensitized OPV, a guest molecule capable of rapid singlet−triplet intersystem crossing is added to the donor layer in order to sensitize triplets on the fluorescent donor host. In this configuration, photogenerated host singlets undergo energy transfer to a triplet-sensitizing guest, which rapidly forms triplets that are subsequently transferred back to the long-lived host triplet state. In prior demonstrations, the guest is a heavy-metal-centered phosphor capable of rapid intersystem crossing.[16−27] For example, Luhman and Holmes used a host−guest pairing of *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPD) and tris[2-phenylpyridinato-C2,N]iridium(III) ($Ir(ppy)_3$) to demonstrate an increase in L_D from (6.5 ± 0.3) to (11.8 ± 0.6) nm at 5% doping.[18] Rand et al. investigated the host−guest pairing of phenyl-substituted poly(*p*-phenylene vinylene) (PPV) and platinum octaethylporphyrin (PtOEP) and demonstrated an increase in L_D from (4 ± 1) to (9 ± 1) nm for an optimal doping of 5%.[19] This approach has been further applied to bulk heterojunction OPVs realizing significant increases in photocurrent.[20] Similarly, Angel and Tang incorporated PtOEP into poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene (MEH-PPV) and found an increase in L_D from 2.0 to 5.0 nm.[26] Despite prior demonstrations of enhanced device performance using triplet sensitizers, there are several challenges associated with quantifying L_D in these systems.

Previous demonstrations of triplet-sensitized OPVs have often relied on fitting device external quantum efficiency (η_{EQE}) spectra to extract L_D. Device-based methods are employed as the dark host triplets are not accessible using conventional photoluminescence (PL) quenching measurements.[28−31] Values of L_D extracted from fitting η_{EQE} spectra are frequently underestimates due to unaccounted geminate recombination losses.[32−34] A second challenge with previous work is the open question of how large an increase in L_D is practically possible. Prior reports have not separately characterized the triplet L_D of the fluorescent host nor

Received: November 27, 2019
Revised: January 16, 2020
Published: February 3, 2020

https://dx.doi.org/10.1021/acs.jpcc.9b11091
J. Phys. Chem. C 2020, 124, 3489−3495

typically is there discussion of how much exciton transport occurs via the triplet of the sensitizer. To address these issues, a device-based measurement technique for L_D is employed that is not impacted by unknown geminate recombination losses.[35] This approach has been previously vetted against PL-based methods for luminescent systems, showing good agreement for the extracted values of L_D. We further characterize a lower-limit on the diffusion length of the host triplet allowing some assessment of the upper limit for L_D in sensitized systems.

Here, exciton transport is examined for a composite donor layer consisting of a metal-free phthalocyanine (H_2Pc) host and a copper phthalocyanine (CuPc) sensitizer as a function of the composition (Figure 1). The host H_2Pc has a singlet

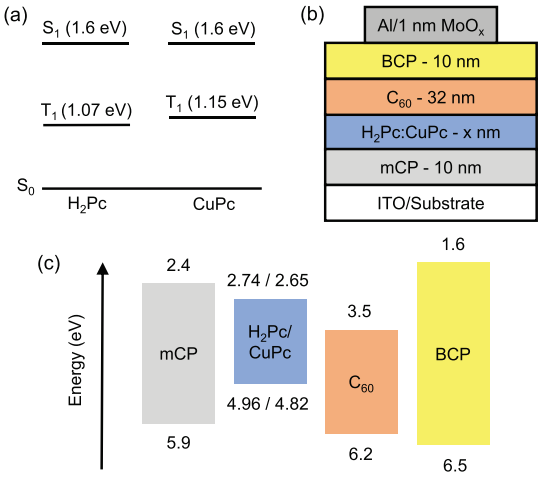


Figure 1. (a) Singlet (S) and triplet (T) excitonic energy levels of H_2Pc and CuPc. (b) Device architecture for H_2Pc:CuPc–C_{60} planar heterojunction OPVs. The H_2Pc:CuPc thickness x varies from 8 to 28 nm. (c) Energy-level diagram for the devices in (b). The LUMO levels are estimated using the optical gap for mCP and taken from prior reports of inverse photoelectron spectroscopy for H_2Pc, CuPc, C_{60}, and BCP.

energy level of E_S = 1.6 eV above the ground state calculated as the cut-off wavelength of the extinction coefficient and a triplet energy level E_T = 1.07 eV.[36] The guest CuPc has nominally the same singlet energy as H_2Pc and a slightly larger triplet energy E_T = 1.13–1.15 eV, permitting singlet energy transfer to CuPc and subsequent triplet energy transfer to H_2Pc.[36,37] Using time-resolved two-photon photoemission, Dutton and Robey have previously shown that intersystem crossing in CuPc occurs on a subpicosecond timescale.[38] Using transient absorption spectroscopy, Caplins et al. found that in vapor-deposited thin films of CuPc, intersystem crossing occurs about 10^4 times faster than natural decay.[39] This suggests that the triplet yield in CuPc thin films is near-unity, allowing CuPc to act as a potentially efficient sensitizer to populate triplets in H_2Pc. The use of CuPc as a sensitizer is advantageous in that unlike Ir- and Pt-phosphors, CuPc is highly absorbing, meaning the inclusion of the sensitizer does not reduce donor layer absorbance.

EXPERIMENTAL SECTION

Figure 1b shows the OPV layer structures of interest for this study with a host–guest donor layer of H_2Pc:CuPc and an acceptor layer of C_{60}. The corresponding highest occupied and lowest unoccupied molecular orbital (LUMO) energy levels for each layer are shown in Figure 1c.[40–42] Layers of 1,3-bis(*N*-carbazolyl)benzene (mCP) and bathocuproine (BCP) act as exciton blocking layers to prevent quenching at the electrodes. A 1 nm-thick layer of MoO_x is deposited before the 100 nm-thick Al cathode to increase the cathode work function and reduce the built-in electric filed, minimizing exciton bulk ionization process at short circuit.[35,43,44]

Layers were deposited by high vacuum thermal evaporation on indium-tin-oxide-coated glass substrates with a sheet resistance of 8–12 Ω/□. Substrates were sequentially cleaned with tergitol, acetone, and isopropanol, followed by exposure to UV–ozone ambient for 15 min prior to deposition. The circular device active area is 0.785 mm^2 defined by the cathode area. The materials mCP (99.5%), CuPc (99%), $Ir(ppy)_3$ (99%), and tris(4-carbazoyl-9-ylphenyl)amine (TCTA) (99.5%) were purchased from Luminescence Technology Corporation. C_{60} (99.9%) was purchased from MER Corporation. H_2Pc (98%) was purchased from Sigma-Aldrich Corporation. BCP (98%), MoO_3 (99%), and Al shot (99.999%) were purchased from Alfa Aesar. NPD (99%) was synthesized by the Dow Chemical Company and purified by temperature-gradient sublimation.[45,46]

Thin film PL spectra were collected under pumping by a laser at a wavelength of λ = 405 nm using a Princeton Instruments FERGIE spectrometer. Low temperature measurements were carried out in a liquid He optical cryostat. Film thickness, optical constants (except H_2Pc and CuPc), and reflectivity spectra were measured using a J.A. Woollam variable-angle spectroscopic ellipsometer. Reflectivity measurements were performed at an incident angle of 15° to the substrate normal. The optical constants of neat H_2Pc and CuPc were extracted by fitting transmission (at normal incidence) and reflectance (at 15°) using an optical transfer matrix model.[47] The optical constants of mixed H_2Pc:CuPc films were calculated using a linear superposition based on neat-film optical constants. Device external quantum efficiency curves were measured under illumination from a 300 W Oriel Xe lamp equipped with a Cornerstone 130 1/8 m monochromator and a Stanford Research Systems SR540 optical chopper. Error bars for L_D represent a 95% confidence interval extracted from fitting.

RESULTS AND DISCUSSION

Prior to characterizing exciton diffusion in OPVs based on mixtures of H_2Pc:CuPc, it is important to first verify that the triplet of the host is in fact being pumped via energy transfer from CuPc. A measurement of increased L_D in mixtures alone is not sufficient as the lifetime and diffusivity of the H_2Pc singlet are both likely a function of the composition.[48–53] To first test the singlet energy transfer from H_2Pc to CuPc, PL spectra for a neat film of H_2Pc (~300 nm) and an equal mixture of H_2Pc:CuPc (~200 nm) were compared (Figure 2). In the neat film, H_2Pc is found to exhibit a measurable PL at temperatures of T = 300 K and T = 10 K with an increased intensity as the temperature is reduced.[54] In contrast, no PL is detected from the mixture, suggesting that excitons generated on H_2Pc are effectively transferred to the CuPc guest. Further considering the ultrafast intersystem crossing rate (~500 fs) of CuPc, it is likely that all the singlets are converted into CuPc triplets.[38,39] We further argue that given the exothermic energetic alignment for triplet energy transfer from CuPc to H_2Pc, a thermodynamically significant H_2Pc triplet population should accumulate because of the sensitization effect.

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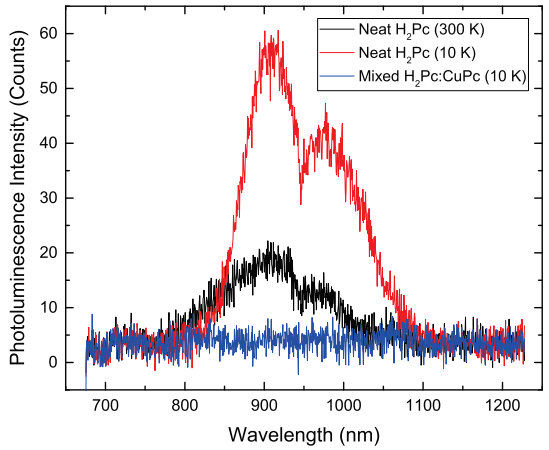

Figure 2. Thin film PL spectra for neat H_2Pc (~300 nm) and films of H_2Pc doped with 50 vol % CuPc (~200 nm) films on Si substrates. The pump wavelength is λ = 405 nm.

As noted earlier, the L_D of dark excitons is often estimated by fitting η_{EQE} spectra.[29,31,47,55] Photoconversion can be divided into four sequential processes each with a corresponding efficiency namely optical absorption (η_A), exciton diffusion and dissociation (η_D), charge-transfer (CT) state separation (η_{CS}), and free carrier collection (η_{FC}). While $\eta_{FC} \approx 100\%$ under short-circuit conditions, η_{CS} is not rigorously unity, and charge separation competes with geminate recombination.[33−35,56−58] As such, assuming $\eta_{CS} \approx 100\%$ and fitting η_{EQE} only for optical generation (η_A) and exciton diffusion (η_D) can yield an underestimate to the material-relevant L_D. Here, an alternate device-based method is applied that is based on fitting ratios of the donor-to-acceptor internal quantum efficiency (η_{IQE}) as a function of the layer thickness. The η_{IQE} is the ratio of the number of collected charge carriers to the number of absorbed photons, which equals to η_{EQE} divided by η_A. This method circumvents unknown recombination losses as losses associated with the CT state are identical for the donor and acceptor, and hence cancel in the ratio to yield material-relevant L_D as[35]

$$\frac{\eta_{IQE}^{D}}{\eta_{IQE}^{A}} = \frac{\eta_{D}^{D}\cdot\eta_{CS}}{\eta_{D}^{A}\cdot\eta_{CS}} = \frac{\eta_{D}^{D}}{\eta_{D}^{A}} \quad (1)$$

where the superscripts D and A denote donor and acceptor efficiencies, respectively. Figure 3a,b shows η_{EQE} spectra collected at short circuit for the device in Figure 1b with donor layers consisting of either neat H_2Pc or 80 vol % H_2Pc:20 vol % CuPc, respectively. Figure 3c,d shows the absorption efficiency spectra (η_A) of the active layers calculated using an optical transfer matrix formalism.[47] Comparing the η_{EQE} spectra, the doped device shows an increase in the efficiency of the donor relative to the acceptor. The interfacial CT state energies (E_{CT}) are nominally ~1.06 and ~1.08 eV for H_2Pc-C_{60} and CuPc−C_{60}, respectively.[59,60] Prior work has suggested that despite a potentially small energetic driving force, triplet dissociation is facilitated by an entropic driving force or the presence of an interfacial dipole that may locally impact the energetic alignment.[60]

In order to calculate the change in L_D responsible for the observed increase in donor η_{EQE}, Figure 4a,b shows the η_{IQE} spectra for the devices of Figure 3. The donor-to-acceptor η_{IQE} ratios of Figure 4c are calculated by dividing η_{IQE} at λ = 700 nm (primarily donor absorption) by that at λ = 340 nm (primarily acceptor absorption). Through eq 1, η_D ratios can be determined as a function of donor thickness and iteratively fit for the donor and acceptor layer L_D. With knowledge of L_D, the absolute η_{EQE} can be fit using the previously unknown value of η_{CS} as a fit parameter except for a range of λ = 410−550 nm, where prior work has noted a possible relaxation bottleneck for bulk CT state excitons in C_{60}.[35] The associated fits of η_{EQE} are shown in Figures S4−S10.

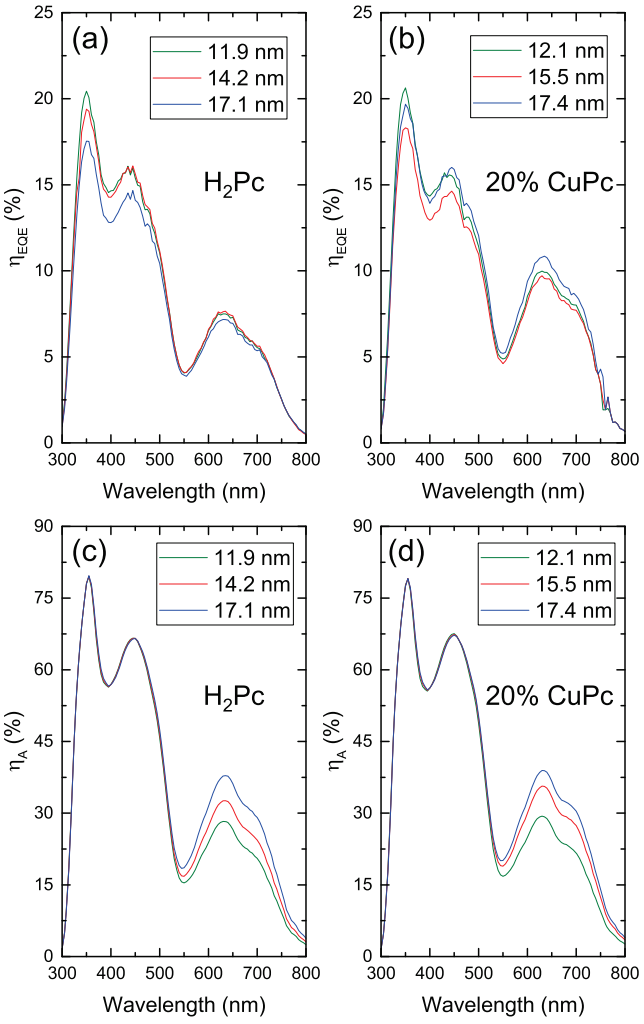

Figure 3. Measured external quantum efficiency (η_{EQE}) and calculated absorption efficiency (η_A). The η_{EQE} measured at short circuit as a function of the donor layer thickness for devices containing a donor layer of H_2Pc (a) or 80 vol % H_2Pc:20 vol % CuPc (b). (c,d) Calculated η_A for the devices in (a,b), respectively.

Using the aforementioned device-based method, donor and acceptor L_D values are extracted as a function of the donor layer composition, as shown in Figure 5. It is worth noting that while the dissociation efficiency of the donor−acceptor CT state may vary in compositions, this would not impact the ability to extract L_D in a self-consistent manner. The donor L_D increases from a value of (8.5 ± 0.4) nm for a neat film of H_2Pc to a maximum of (13.4 ± 1.6 nm) at 20 vol % CuPc (Figure 4c). For compositions beyond the maximum, the value of L_D decreases with the increasing CuPc content. This trend likely suggests a trade-off between exciton transport on different states in the donor layer. If the guest concentration is small enough that the separation between H_2Pc and CuPc

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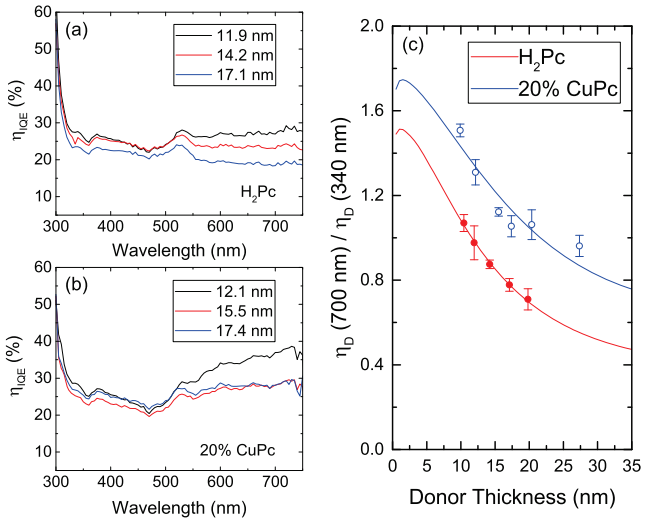

Figure 4. Extracting intrinsic L_D based on fitting thickness-dependent ratios of the internal quantum efficiency. The η_{IQE} spectra calculated as a function of the donor layer thickness from the η_{EQE} for devices containing a donor layer of H_2Pc (a) or 80 vol % H_2Pc:20 vol % CuPc (b). (c) Calculated diffusion efficiency ratio (λ = 700 nm to λ = 340 nm) as a function of the donor layer thickness for the devices (a,b), respectively. The value of L_D is extracted from the fit (solid lines).

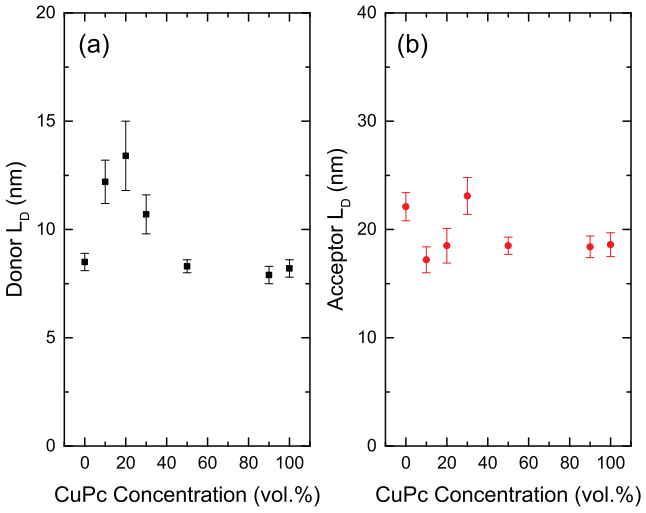

Figure 5. Extracted L_D of the donor and acceptor as a function of the donor concentration. The L_D values of the donor (a) and acceptor (b) are extracted simultaneously based on fitting thickness-dependent ratios of donor−acceptor η_{IQE}.

molecules exceeds the singlet exciton L_D and host−guest Förster radius, the efficiency of energy transfer to the guest is reduced and diffusion occurs via the H_2Pc singlet. If instead the host (H_2Pc) concentration is small, triplets are confined to and diffuse on CuPc. It is thus reasonable to expect the optimum composition to be H_2Pc-rich because the short-range Dexter energy transfer of triplets from CuPc to H_2Pc is likely the rate-limiting step. The C_{60} acceptor L_D in Figure 5b shows no systematic variation in composition and is comparable to previously reported values.[35] This suggests that only the diffusion efficiency of the donor layer is impacted by changes in the donor layer concentration.

It is interesting that the L_D values of neat H_2Pc and CuPc are comparable despite the difference in the diffusing exciton spin state. It was previously reported that the exciton lifetime in CuPc is about 35 times larger than that of H_2Pc.[39] This suggests that the corresponding diffusion coefficient for triplet excitons in CuPc is ∼1/35 that of singlet excitons in H_2Pc. This difference may reflect the short-range Dexter energy transfer responsible for triplet diffusion. It also reemphasizes the need to populate the longer lived triplet states in a fluorescent host rather than using the shorter lived triplets present in materials with rapid intersystem crossing. Based on the extracted L_D value of 8.2 nm and the previously reported lifetime 8.6 ns, the diffusion coefficient for triplets in CuPc is calculated to be 7.8×10^{-5} cm^2/s, comparable to previous measurements of triplet diffusion.[13,39]

An important question is whether the observed increase in the donor layer L_D fully utilizes the long-lived triplets in H_2Pc. Several factors must be considered when answering this question including an assessment of the intrinsic triplet L_D in H_2Pc. A lower limit on the triplet L_D in a neat film of H_2Pc is determined using a photocurrent measurement capable of selectively injecting triplets.[28,61] The relevant device architectures are shown in Figure 6a,b, while the associated molecular orbital energy levels are shown in Figure S11a.[36,40−42,62−64] In these structures, a mixed layer of NPD:$Ir(ppy)_3$ is optically pumped with photogenerated $Ir(ppy)_3$ triplets (E_T = 2.4 eV) transferred to the NPD triplet state (E_T = 2.3 eV). Triplets that

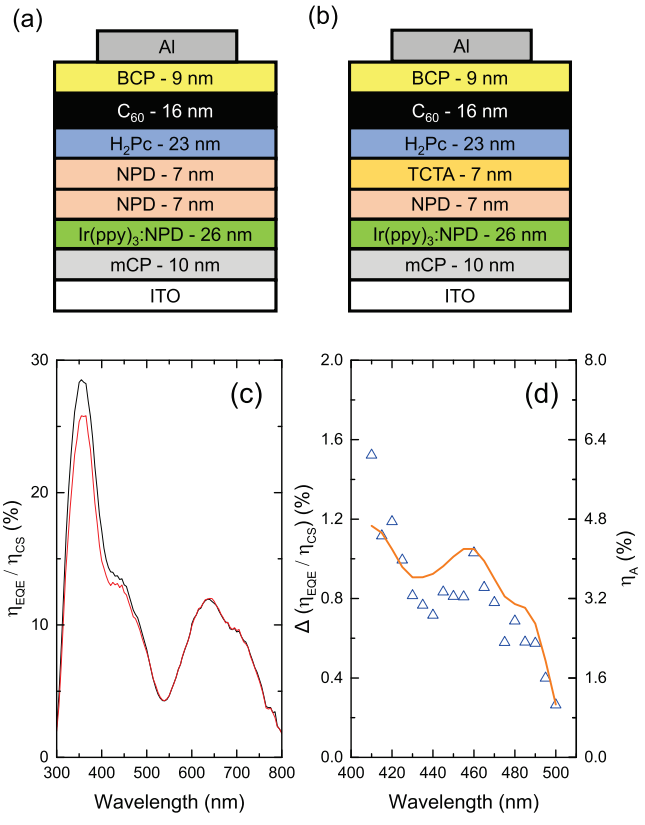

Figure 6. Extraction of the triplet diffusion length of H_2Pc. Relevant architectures enabling direct injection into the H_2Pc triplet both without (a) and with (b) a triplet blocking layer of TCTA. (c) Experimental η_{EQE}/η_{CS} spectra for devices without (black line) and with a (red line) triplet blocker. The triplet injection layer is a uniform mixture of $Ir(ppy)_3$:NPD. (d) Calculated $\Delta(\eta_{EQE}/\eta_{CS})$ spectrum (symbols) and the absorption efficiency η_A (solid line) of the $Ir(ppy)_3$:NPD layer with absorption occurring only in $Ir(ppy)_3$.

https://dx.doi.org/10.1021/acs.jpcc.9b11091
J. Phys. Chem. C 2020, 124, 3489−3495

migrate across the adjacent neat layer of NPD are subsequently injected into the triplet state of H_2Pc. Injected triplets that are harvested from H_2Pc will lead to an increase in external quantum efficiency over wavelengths where $Ir(ppy)_3$ absorbs. Extinction spectra for all active materials are shown in Figure S11b. A control architecture is also measured (Figure 6b) where half of the neat NPD layer is replaced with the triplet exciton blocker TCTA (E_T = 2.8 eV), frustrating triplet injection from NPD into H_2Pc. This control structure is used to decouple the direct optical excitation of H_2Pc and C_{60} in Figure 6a.

To extract the triplet L_D of H_2Pc using the architectures of Figure 6, it is necessary to know the number of triplets injected from the neat layer of NPD into H_2Pc and the number of triplets dissociated at the H_2Pc-C_{60} interface. The number of triplets injected can be calculated based on the number of photogenerated triplet excitons in $Ir(ppy)_3$ and the diffusion efficiency of the neat NPD layer. Assuming that all triplets in $Ir(ppy)_3$ are injected into the neat layer of NPD, triplet diffusion in NPD can be modeled using a previously measured value for the diffusion length (L_D = 25 nm), leading to an upper limit on the injected exciton density and ultimately a lower limit on the triplet diffusion length of H_2Pc.[28] The number of triplets dissociated from H_2Pc is thus proportional to the difference in η_{EQE}/η_{CS} between devices with and without the triplet blocker of TCTA. Here, the η_{EQE} is divided by η_{CS} to decouple changes in the geminate recombination loss. The value of η_{CS} can be extracted by simulating the measured η_{EQE} spectra at the donor-absorption using the L_D values of Figure 5. The resulting ratios of η_{EQE}/η_{CS} are shown in Figure 6c for the architectures of Figure 6a,b. In comparing devices with and without a triplet blocking layer, a measurable increase in response is observed between wavelengths of 325 and 500 nm. The increase between 325 and 410 nm reflects absorption on TCTA, NPD, and $Ir(ppy)_3$:NPD, leading to the injection of both singlets and triplets into H_2Pc. Between 410 and 500 nm, the enhancement comes more exclusively from absorption on $Ir(ppy)_3$ and reflects triplet injection into H_2Pc. By fitting the $\Delta\eta_{EQE}/\eta_{CS}$ spectrum in Figure 6d, a lower limit for the triplet L_D of H_2Pc is obtained to be (20.7 ± 5.0) nm.

The value of L_D extracted for the triplet in neat films of H_2Pc may suggest that further gains are possible with further optimization of the sensitization scheme. Since the triplet energy level difference between the host H_2Pc and the guest CuPc is small (~0.06−0.08 eV), reverse energy transfer back to the CuPc triplet state may occur, reducing the overall L_D. Triplet confinement to H_2Pc may be improved by using a sensitizer with higher triplet energy. However, it is also important to point out that the actual situation may be more complicated as the addition of CuPc to H_2Pc will impact the intermolecular packing and spacing between H_2Pc molecules as well as the triplet lifetime. These factors may conspire to set a different upper limit on the H_2Pc triplet L_D in mixed films. Further detailed spectroscopic studies are needed to assess these additional contributions to the maximum achievable value of L_D.

CONCLUSIONS

We characterize exciton transport in triplet-sensitized OPVs based on the mixed donor system of H_2Pc:CuPc as a function of composition. Using an internal quantum efficiency ratio methodology to decouple recombination losses, the composite donor layer L_D is measured as a function of the sensitizer concentration. The measured trend indicates an exciton transport tradeoff between the energy transfer from host singlets to guest singlets and the energy transfer from guest triplets to host triplets. The optimal CuPc concentration is 20 vol % and the donor L_D is increased from (8.5 ± 0.4 nm) to (13.4 ± 1.6 nm). Despite a nearly 60% enhancement, additional gains are likely possible because the triplet L_D of H_2Pc is measured to be >(20.7 ± 5.0) nm. This suggest that there is still room to further exploit long-lived triplets, likely by employing a sensitizer with a higher triplet energy level to promote the formation of host triplets.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b11091.

Reflectivity of planar heterojunction OPVs, diffusion efficiency ratios, external quantum efficiency spectra, and details for triplet diffusion length measurement (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (NSF) Program in Solid-State and Materials Chemistry DMR-1708177. R.J.H. would like to acknowledge support from a Leverhulme Trust Visiting Professorship at the University of Cambridge and a Visiting Fellowship at Clare Hall, University of Cambridge. The authors thank Dr. D. Wayne Blaylock at the Dow Chemical Company for synthesizing NPD.

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