Measurements of Dark Triplet Exciton Diffusion in a Phosphor-Sensitized Organic Photovoltaic Cell

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ABSTRACT

Organic photovoltaic cell performance is limited in part by a short exciton diffusion length (L_D). While state-of-the-art devices address this challenge using a morphology-optimized bulk heterojunction (BHJ), longer L_D would relax domain-size constraints and enable higher efficiency in simple bilayer architectures. One approach to increase L_D is to exploit long-lived triplet excitons in fluorescent materials. Though these states do not absorb light, they can be populated using a host-guest triplet-sensitized architecture. Photogenerated host singlets undergo energy transfer to a guest, which rapidly forms triplets that are transferred back to the long-lived host triplet state. Previous efforts have been focused on Pt- and Ir-based guests. Here, a host-guest pairing of metal-free phthalocyanine (H_2Pc) and copper phthalocyanine (CuPc) is explored, advantageous as the guest also has strong and complementary optical absorption. In optimized devices (20 vol.% CuPc), the short-circuit current is enhanced by 20%. To probe the origin of the enhancement, the exciton L_D is measured using a device-based methodology that relies on fitting ratios of donor-to-acceptor internal quantum efficiency as a function of layer thickness. Compared with the neat H_2Pc, the L_D of the 20 vol.% CuPc doped layer increases from (8.5 ± 0.4) nm to (13.4 ± 1.6 nm), confirming the increased device current comes from enhanced exciton harvesting.

Keywords: Organic Photovoltaic Cells, Triplet Excitons, Triplet Sensitizers, Exciton Diffusion Length

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1. INTRODUCTION

Organic semiconductors typically have a short exciton diffusion length ($L_D \sim 10$ nm) in comparison to the long optical absorption length ($L_A \sim 100$ nm), limiting the performance of planar heterojunction organic photovoltaic cells (OPVs). State-of-the-art devices address this challenge using a morphology-optimized bulk heterojunction (BHJ) to increase exciton harvesting.[1-10] Despite these achievements, a long L_D is desirable since it can relax domain-size constraints and enable higher efficiency in simple bilayer structures. One approach to enhance L_D is to utilize long-lived triplet excitons.[11-16] The challenge in using triplets is that they are typically characterized by very low optical absorption, making them inaccessible under optical pumping.

Prior works have overcome the challenge of optically pumping triplets by using a host-guest triplet-sensitized structure.[16-27] In such a structure, a guest molecule with a heavy metal permitting rapid singlet-triplet intersystem crossing is mixed with a fluorescent host. Under optical pumping, photogenerated host singlets can undergo energy transfer to the guest, which rapidly forms triplets and are subsequently transferred back to the long-lived host triplet state. Previous efforts have been focused on Pt- and Ir-based guests. For example, the incorporation of 5% tris[2-phenylpyridinato-C2,N]iridium(III) ($Ir(ppy)_3$) into N,N'-Bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPD) has been shown to increase L_D from (6.5 ± 0.3) nm to (11.8 ± 0.6) nm.[18] Among several demonstrations based on a polymer host, the doping of phenyl-substituted poly(p-phenylene vinylene) (PPV) with 5% platinum octaethylporphyrin (PtOEP) leads to an increase in L_D from (4 ± 1) nm to (9 ± 1) nm.[19, 20, 26]

Previous work has shown that the presence of Cu in copper phthalocyanine (CuPc) leads to ultrafast singlet-triplet intersystem crossing in ~500 fs, making it a potential triplet sensitizer.[28] It is also advantageous due to strong optical absorption, which means its incorporation as a guest will not reduce donor layer absorbance. Here, a host-guest pairing of metal-free phthalocyanine (H_2Pc) and CuPc is examined in OPVs, and also analyzed in terms of exciton transport. The relevant singlet and triplet exciton energy levels are shown in Fig. 1a, suggesting singlet transfer from H_2Pc to CuPc and triplet transfer from CuPc back to H_2Pc.[29, 30] In this way, optical pumping of H_2Pc singlets leads to the formation of mobile H_2Pc triplets. In order to accurately assess any changes in L_D, a device-based method is employed to accurately probe the diffusion of dark triplets, based on fitting ratios of donor-to-acceptor internal quantum efficiency as a function of layer thickness.[31]

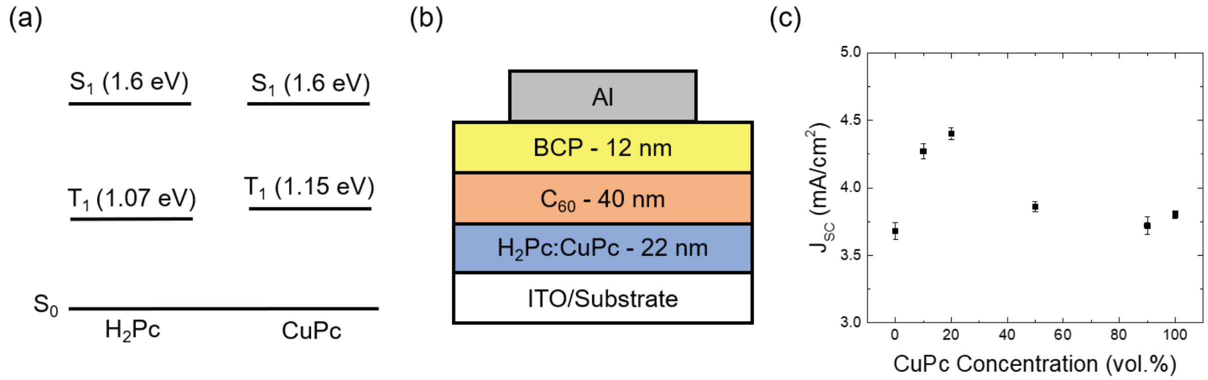

Figure 1. (a) Exciton energy levels and (b) device structure of interest in this work. (c) Short-circuit current density (J_{SC}) for the device in (b) as a function of CuPc concentration (1 Sun AM1.5G).

2. EXPERIMENTAL

1,3-bis(N-carbazolyl)benzene (mCP) (99.5%) and CuPc (99%) were purchased from Luminescence Technology Corporation. H_2Pc (98%) was purchased from Sigma-Aldrich Corporation. C_{60} (99.9%) was purchased from MER Corporation. Bathocuproine (BCP) (98%), MoO_3 (99%) and Al shot (99.999%) were purchased from Alfa Aesar. Devices were constructed on indium-tin-oxide (ITO)-coated glass substrates. Substrates were sequentially cleaned with tergitol, acetone, and isopropanol, before exposure to UV-ozone ambient for 15 min prior to deposition. Layers were grown using high vacuum thermal evaporation at a pressure below 8×10^{-7} Torr. Device active area was defined by the cathode to be 0.785 mm^2. All film thicknesses were measured using a J. A. Woollam spectroscopic ellipsometer. Devices were tested under illumination from a 150 W Oriel Solar Simulator. The short-circuit current was measured using an Agilent Technologies 4155C Semiconductor Parameter Analyzer. For measurements of L_D, external quantum efficiency spectra were measured under illumination from a 300 W Oriel Xe lamp and a Cornerstone 130 1/8-meter monochromator followed by a Stanford Research Systems SR540 optical chopper wheel. Optical constants (except H_2Pc and CuPc) and reflectivity spectra were measured using spectroscopic ellipsometery. 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 formalism.[32] The optical constants of mixed H_2Pc:CuPc films were calculated as a linear superposition. Error bars for L_D represent a 95% confidence interval extracted from fitting data.

3. RESULTS AND DISCUSSION

3.1 Device performance

The role of the sensitizer in impacting device short-circuit current was examined by measuring a series of OPVs with the same layer thicknesses and variable sensitizer concentration (Fig. 1b). In doped devices, the H_2Pc:CuPc layer is the composite donor while C_{60} is the electron acceptor. The BCP layer acts as an exciton blocker to prevent exciton quenching at the Al cathode. The short-circuit current density (J_{SC}) is measured under 1 Sun AM1.5G simulated illumination as shown in Fig. 1c, and increases with doping from the case of a neat H_2Pc donor layer. A plateau is reached at 20 vol.% CuPc, followed by a decrease and leveling off between 50 vol.% CuPc and neat CuPc. Considering the identical device structure and layer thicknesses, and nearly identical optical constants of both donor materials, the change in J_{SC} and hence device external quantum efficiency (η_{EQE}) reflects either improved exciton diffusion in the donor layer or reduced charge carrier recombination. To examine whether the enhancement reflects an increase in donor layer L_D due to triplet sensitizing, a device-based method is used to extract L_D and decouple recombination losses.

3.2 Extraction of donor exciton diffusion length

To elucidate the observed increase in current with addition of the sensitizer, the donor L_D was probed for the neat H_2Pc and the 20 vol.% CuPc doped samples. While for luminescent materials, photoluminescence (PL)-based techniques are commonly used to extract L_D, these techniques are not applicable to the dark triplets of interest here.[14, 33, 34] While device-based methods have been previously applied to probe triplet diffusion, these methods are limited by unknown carrier recombination losses, frequently making them underestimates.[18, 32, 35-37] Here, an alternate device-based method is applied that is based on fitting ratios of donor-to-acceptor internal quantum efficiency as a function of layer thickness. This method is capable of decoupling recombination losses to yield an intrinsic materials-relevant L_D.[31] Photoconversion can be divided into four key processes namely optical absorption (η_A), exciton diffusion and dissociation (η_D), charge transfer (CT) state separation (η_{CS}) competing with geminate recombination loss, and free carrier collection (η_{FC}) competing with non-geminate recombination loss. Prior work has shown that in many systems, η_{FC} is unity at short-circuit,[36, 37] leaving η_{CS} as the unknown limiting efficiency. Important however is prior work that has demonstrated the equivalence of geminate recombination losses for excitons originating on the donor and acceptor.[38] These results suggest

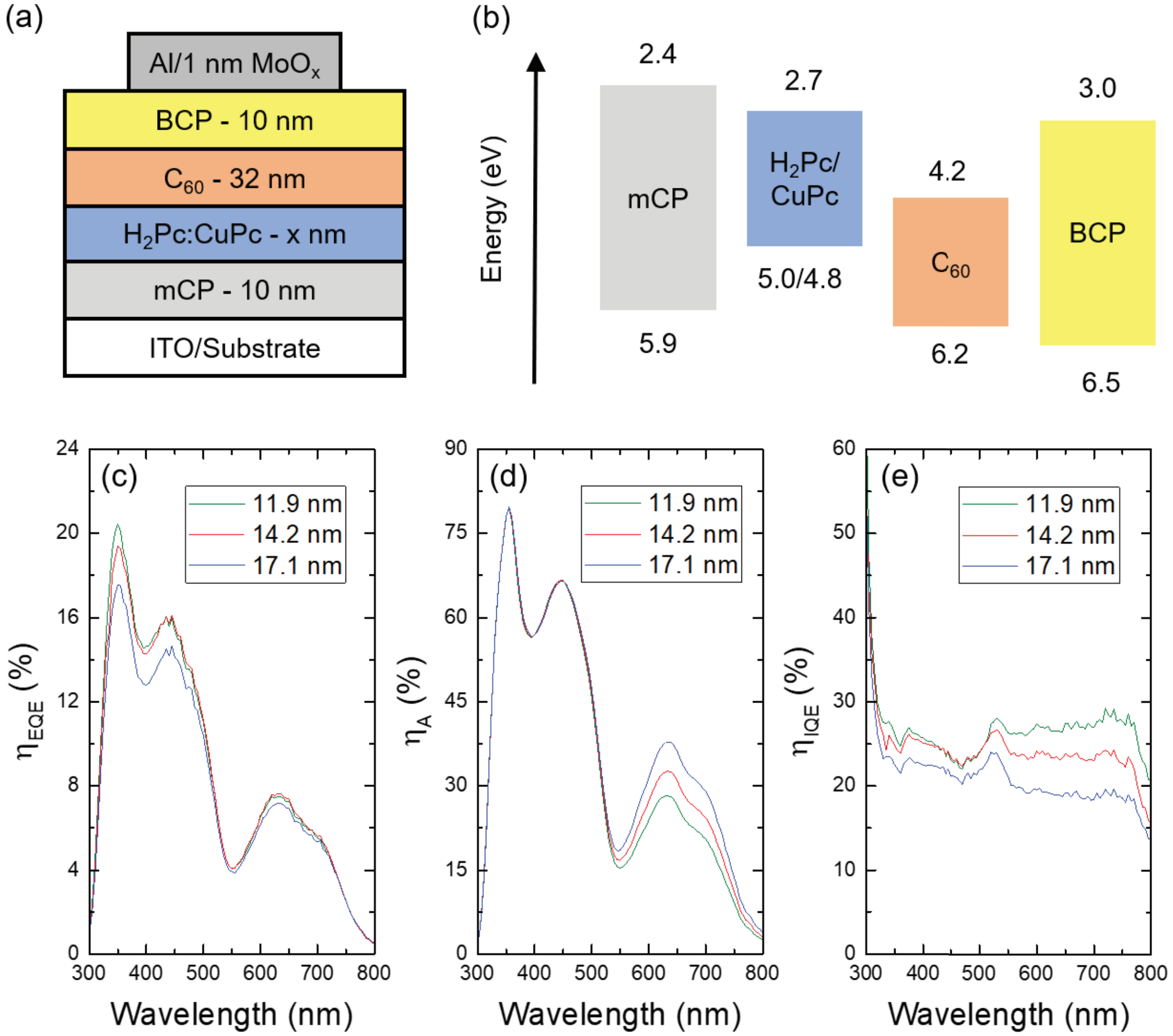

Figure 2. (a) Device structure and (b) energy level diagram for the measurement of L_D. Example data taken from a device with a donor layer of H_2Pc, (c) external quantum efficiency (η_{EQE}), (d) absorption efficiency (η_A), and (e) internal quantum efficiency (η_{IQE}). The legend in each of (c)-(e) reflects changes in donor layer thickness.

that a ratio of donor-to-acceptor internal quantum efficiency (η_{IQE}) can thus cancel the unknown η_{CS} and will only depend on η_D at short circuit, where η_{IQE} is defined as η_{EQE} divided by η_A:

$$\frac{\eta_{IQE}^{D}}{\eta_{IQE}^{A}} = \frac{\eta_{D}^{D}\cdot\eta_{CS}}{\eta_{D}^{A}\cdot\eta_{CS}} = \frac{\eta_{D}^{D}}{\eta_{D}^{A}} \tag{1}$$

By fitting the ratio of donor-to-acceptor internal quantum efficiency for L_D, we are fitting the ratio of donor-to-acceptor exciton diffusion and dissociation efficiency and extracting intrinsic L_D for donor and acceptor simultaneously.

The device architecture (Fig. 2a) used for the extraction of L_D includes a wide-energy gap exciton blocking layer of mCP to prevent exciton quenching at the donor-anode interface, and a more accurate measurement of L_D. The corresponding highest occupied (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels for each layer can be seen in Fig. 2b.[31, 39] A 1-nm-thick layer of MoO_x is deposited under the cathode to increase the work function and decrease the built-in electric field, reducing bulk ionization at short circuit.[31, 40, 41] Figure 2c-e show the data used to calculate the η_{IQE} and ultimately L_D, of H_2Pc as an example of the methodology. The η_A spectra of the active layers, as shown in Fig. 2d, are calculated using an optical transfer matrix model.[32] By dividing η_{EQE} (Fig. 2c) by η_A, η_{IQE} spectra are obtained for different donor layer thicknesses, as shown in Fig. 2e. The donor-to-acceptor η_{IQE} ratios are then determined by dividing the η_{EQE} at $\lambda = 700$ nm (primarily donor absorption) by that at $\lambda = 340$ nm (primarily acceptor absorption). It should be noted that the range of $\lambda = 410$-550 nm should not be used for calculation of η_{IQE} ratios since prior work indicates a possible relaxation bottleneck for bulk CT state excitons in C_{60}, which leads to an overestimated fit of η_{EQE}.[31] Through Eq. 1, η_D ratios are obtained through η_{IQE} ratios as a function of donor thickness and the recombination losses are decoupled. These ratios can be iteratively fit to extract the intrinsic donor and acceptor L_D, as shown in Fig. 3. As the CuPc concentration increases to 20 vol.%, donor L_D increases from (8.5 ± 0.4) nm to (13.4 ± 1.6 nm), almost a 60% increase over the neat

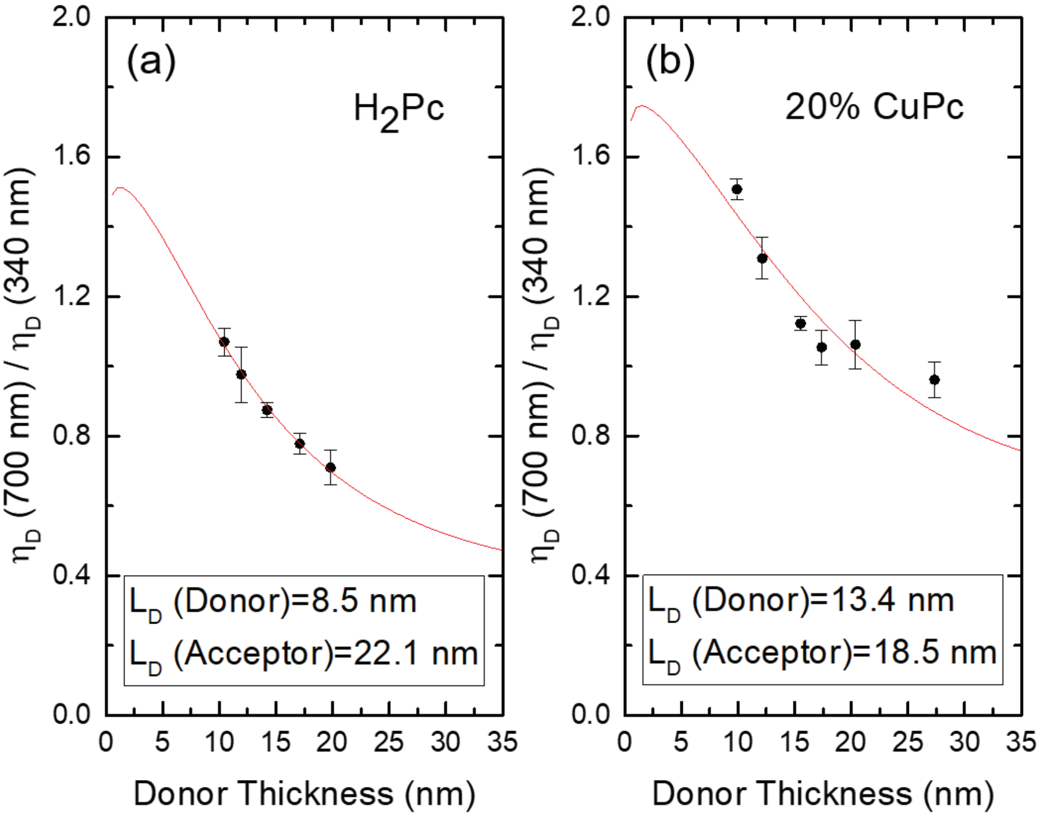

Figure 3. Extraction of materials-relevant L_D by fitting ratios of donor-to-acceptor internal quantum efficiency as a function of layer thickness for devices with (a) the neat H_2Pc layer and (b) the 20 vol.% CuPc doped layer.

H_2Pc. The extracted C_{60} L_D values are comparable to the previously reported values.[31] The significant increase in donor L_D indicates the effect of triplet sensitizer and the contribution to the measured J_{SC}.

4. CONCLUSION

Long-lived triplets are frequently inaccessible under optical pumping due to the spin conservation. A triplet sensitizer with ultrafast intersystem crossing and proper aligned energy levels can efficiently populate host triplets. A host-guest pairing consisting of H_2Pc and CuPc is studied in this work, extending the concept of triplet-sensitization to more broadly absorbing active materials. Devices based on H_2Pc:CuPc-C_{60} show an increase in short-circuit current density with doping of 20 vol.% CuPc relative to the case of a neat H_2Pc donor layer. A plateau in current occurs at 20 vol.% CuPc, followed by a decrease and leveling off between 50 vol.% CuPc and neat CuPc. To elucidate the origin of the observed increase in current with addition of the sensitizer, the donor L_D was probed for the neat H_2Pc and 20 vol.% CuPc doped samples using a device-based method based on fitting ratios of donor-to-acceptor internal quantum efficiency as a function of layer thickness. The donor L_D increases from (8.5 ± 0.4) nm to (13.4 ± 1.6 nm) with incorporation of 20 vol.% CuPc over the case of neat H_2Pc. This significant increase suggests the observed improvement in device performance comes due to the inclusion of the triplet sensitizer.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support by National Science Foundation (NSF) Solid-State and Materials Chemistry DMR-1708177.

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