

Letter

Organic solar cells with sensitized phosphorescent absorbing layers

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ABSTRACT

We demonstrate an increase of the exciton diffusion length (L_D) of a fluorescent donor layer via the process of sensitized phosphorescence, whereby initially generated singlet excitons are transferred to triplet excitons via a properly chosen dopant molecule. Using a poly(*p*-phenylene vinylene) host doped with the phosphorescent molecule platinum octaethylporphyrin, L_D increases from 4 ± 1 to 9 ± 1 nm for an optimal doping of 5 wt%. As a result of the increased L_D , the photocurrent from the doped layer increases by 40%. By doping with the fluorescent, non-metalated analogue octaethylporphyrin, a reduction in photocurrent is shown, providing further evidence of the sensitized phosphorescence mechanism.

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Recently, the power conversion efficiency of organic photovoltaics has progressed rapidly, offering new potential as a low-cost renewable energy source, and driven primarily by the development of new materials, device architectures, and processing techniques [1–6]. In an organic semiconductor, the absorption of a photon results in the creation of a bound electron-hole pair, or exciton, that must diffuse to a donor–acceptor interface to dissociate into free charge carriers. Because exciton diffusion lengths, L_D , are typically on the order of 3–10 nm for singlet excitons [2,7], the major bottleneck for achieving high efficiency is in balancing the low L_D while still achieving thick enough layers to absorb most of the incident light. In fact, the bulk heterojunction (BHJ) device concept, whereby the donor and acceptor materials are deposited simultaneously to form an interpenetrated donor–acceptor interface, was created in order to sidestep this tradeoff

[8,9]. However, it is difficult to achieve a very fine phase separation, on the order of a few L_D , while at the same time preserving the good charge transport required for low resistance, efficient cells. If L_D can be increased, efficiencies will also increase [7,10], and the strict requirements for phase separation of blends can be relaxed. One method that should be able to yield larger L_D is to use molecules which have efficient intersystem crossing (ISC), in order to convert singlet excitons into triplet excitons. Because the decay of spin 1 triplet states to the spin 0 singlet ground state is forbidden, the lifetime of triplet excitons is many orders of magnitude greater than singlet state lifetimes which are on the order of ns. Then, since $L_D = \sqrt{D\tau}$, where D is the exciton diffusivity and τ its lifetime, an overall increase in L_D is expected, which should allow for the harvesting of those excitons generated further from a donor–acceptor interface. However, triplets are virtually non-existent in optically excited fluorescent materials, as both direct generation by light as well as ISC from singlets are inefficient processes.

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Organic photovoltaic devices utilizing phosphorescent materials have previously been demonstrated, either by employing directly a phosphorescent small molecular or polymer layer [11–14], or by inducing phosphorescence in a fluorescent host via a proximity effect of a heavy-metal-atom containing phosphor dopant [15]. However, because phosphorescent organic semiconductors are typically characterized by low mobilities and absorption that do not overlap well with the solar spectrum [13], their use as active, absorbing layers may be difficult to realize. One notable exception [2] is the acceptor C_{60} , which has a high charge carrier mobility of $5 \times 10^{-2} \text{ cm}^2/\text{Vs}$, and $L_D \approx 40 \text{ nm}$ owing to its near unity ISC efficiency [16], albeit with an absorption spectrum still focused in the blue wavelength range.

Here, we demonstrate enhanced photocurrent from a fluorescent material via the process of sensitized phosphorescence. We employ a host:guest system where a fluorescent host material continues to be used for light absorption as well as for charge and exciton transport. The guest serves only to convert initially generated host singlet excitons into triplet excitons, as its low concentration prevents efficient transport and absorption. An advantage of this approach to create triplet excitons on a fluorescent host stems from the fact that due to the lack of an efficient triplet decay pathway, triplet states in fluorescent materials [17,18] generally possess significantly longer lifetimes compared with phosphors containing heavy-metal atoms [19] (e.g. ms compared to μs). To allow for the above processes to occur, the host:guest system needs to obey the following criteria: First, that the lowest excited singlet state of the dopant is lower than that of the host material ($S_{1,\text{dopant}} < S_{1,\text{host}}$), and there is sufficient overlap between the emission of the host and absorption of the guest to allow for efficient singlet energy transfer (SET). Second, that the triplet energy of the dopant molecule is greater than that of the host ($T_{1,\text{dopant}} > T_{1,\text{host}}$) for efficient triplet energy transfer (TET) to occur. In addition, care should be taken to allow for efficient charge transport of photogenerated carriers through the host material. Therefore, an additional criterion for a donor material is that the highest occupied molecular orbital (HOMO) of the dopant is greater than that of the host to prevent holes from being trapped on the guest material which would ultimately reduce photocurrent. In the case of an acceptor material, care should be taken that the lowest unoccupied molecular orbital of the dopant is lower than that of the host material to prevent electron trapping.

To demonstrate that the process of sensitized phosphorescence can be used to increase the photocurrent of an absorbing layer, we use as an example the phenyl-substituted poly(*p*-phenylene vinylene) (PPV) donor polymer Super Yellow (SY) doped with the phosphorescent molecule platinum octaethylporphyrin (PtOEP). Furthermore, we investigate the effect of doping with the Pt-free analogue octaethylporphyrin (OEP) to demonstrate the opposite effect: a dopant that allows SET but not TET is expected to actually reduce the photocurrent. Fig. 1a shows the absorption (Shimadzu UV-1601PC) and emission (Shimadzu RF-5301PC) of a pure SY film as well as films doped with PtOEP, whereas Fig. 1b shows SY films

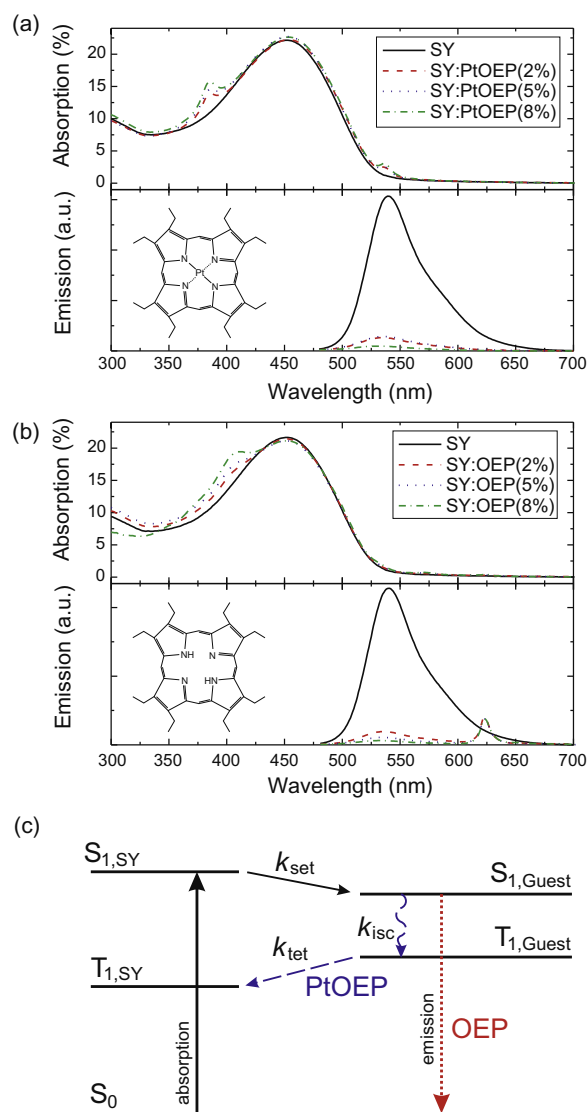


Fig. 1. (a) Absorption (top panel) and photoluminescence (PL) (bottom panel) of 15 nm thick SY and SY:PtOEP thin films with various compositions. The molecular structure of PtOEP is shown as an inset to the bottom panel. (b) Absorption (top panel) and PL (bottom panel) of 15 nm thick SY and SY:OEP thin films with various compositions. The molecular structure of OEP is shown as an inset to the bottom panel. (c) The formation pathways of excitons generated in doped SY. Following absorption in SY to excite a molecule from the ground state (S_0) to the first excited singlet state ($S_{1,\text{SY}}$) there is singlet energy transfer to the guest at a rate k_{set} . For the guest PtOEP (blue dashed arrows), intersystem crossing converts singlet excitons to triplet excitons from $S_{1,\text{Guest}}$ to $T_{1,\text{Guest}}$ at a rate k_{isc} . Finally, the lower triplet energy of SY ($T_{1,\text{SY}}$) quenches the PtOEP triplets with a rate k_{tet} . In the case of an OEP guest (red dotted arrow), the lack of an efficient ISC pathway results in singlet emission.

doped with OEP. The absorption shoulders of PtOEP and OEP are present in the doped films, at wavelengths of $\lambda = 385$ and 535 nm for PtOEP and at $\lambda = 410 \text{ nm}$ for OEP, and the intensity of these peaks increases with doping concentration. The SY emission (excitation at $\lambda = 385 \text{ nm}$), with its peak at $\lambda = 540 \text{ nm}$, is quenched rapidly as a result of the introduction of either dopant. Significantly, PtOEP

phosphorescence [20] at $\lambda = 650$ nm is not present, whereas OEP fluorescence at $\lambda = 625$ nm is observed. This suggests the excitonic pathways illustrated schematically in Fig. 1c, where for the case of PtOEP there is efficient SET from SY to PtOEP molecules, followed by ISC, and finally TET back to SY owing to the lower triplet energy of SY (≈ 1.6 eV) compared to that of PtOEP (≈ 1.9 eV), a phenomenon which has been shown previously for PtOEP in PPV hosts [21]. In the case of OEP, SET onto the OEP dopant occurs, but since OEP is a fluorescent molecule, ISC efficiency is very low and singlet OEP emission is observed.

For the demonstration of sensitized phosphorescence in a solar cell, we use the following device structure: indium–tin–oxide (ITO)/poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT) (30 nm)/SY (15 nm)/C₆₀ (30 nm)/bathocuproine (BCP) (8 nm)/Al (80 nm). Here, ITO/PEDOT serves as the anode, SY as the donor layer, C₆₀ as the acceptor layer, BCP as an exciton blocking layer, and Al as the cathode. The reason for employing only a 15 nm thick SY layer is because the use of thicker layers led to a rapidly increasing series resistance for the device, reducing the fill factor (FF) as well as, and even more significantly, the short circuit current density J_{SC} . The ITO coated glass substrates were solvent cleaned followed by UV/O₃ treatment for 10 min. The PEDOT (H.C. Starck, Baytron P VPAI4083) solution was spincoated at 3000 rpm for 60 s, followed by baking at 120 °C. The SY was dissolved in toluene at a concentration of 1.7 mg/ml, with doping of PtOEP or OEP by weight, followed by spincoating at 2000 rpm for 60 s. The C₆₀, BCP, and Al layers were then deposited in an ultrahigh vacuum chamber (base pressure $< 5 \times 10^{-9}$ Torr). The device area was measured with an optical microscope, with an average area of 3.3 mm². The current density vs. voltage (J – V) characteristics were measured using an Agilent 4156C parameter analyzer with illumination from a LOT-Oriel 1000 W Xe arc lamp fitted with

AM 1.5D filters. Calibration was performed by a KG3 band pass filter and a calibrated Si detector.

The schematic energy diagram of this device is shown in the inset to Fig. 2, where we also show the J – V characteristics of devices with undoped SY, SY:PtOEP(5%) and SY:OEP(5%) donor layers in the dark and under 100 mW/cm² AM1.5D simulated solar illumination. The undoped SY-based device has $J_{SC} = 3.2$ mA/cm², open circuit voltage $V_{OC} = 0.86$ V, FF = 0.54, and power conversion efficiency $\eta_p = 1.5\%$. The doped devices have the same value of V_{OC} , which indicates that the host SY acts as the charge conducting material, a property which is expected for films containing a low concentration of dopant ($< 10\%$) and also owing to the shallower HOMO of SY (5.2 eV) with respect to that of either PtOEP (5.3 eV) or OEP (5.5 eV). The PtOEP-doped device has a dark current almost identical to that of the undoped device, and $J_{SC} = 3.5$ mA/cm², FF = 0.52, and $\eta_p = 1.6\%$ under illumination. In this case, the photocurrent is increased by almost 10%, whereas the FF is slightly decreased, which could indicate that the presence of the PtOEP dopant molecule interrupts charge carrier transport in the SY matrix, making the collection of photogenerated charges more difficult. For the case of 5% OEP doping, $J_{SC} = 2.8$ mA/cm², FF = 0.41, and $\eta_p = 1\%$. Here, the OEP dopant increases the series resistance of the cell, as reflected in the lower dark current at $V \geq 0.7$ V as compared to the other devices. This has the effect of reducing the FF, but does not significantly impact J_{SC} , as an equally reduced photocurrent can be observed even for negative voltages, where photogenerated carriers are efficiently extracted by the applied field.

To understand better the influence of the dopant and whether sensitized phosphorescence plays a role in the device operation, we show in Fig. 3 the dependence of J_{SC} on dopant concentration for either PtOEP or OEP doping. It should be noted that the roughness and therefore interfacial area of the donor–acceptor heterojunction does not increase with doping concentration, as measurements by

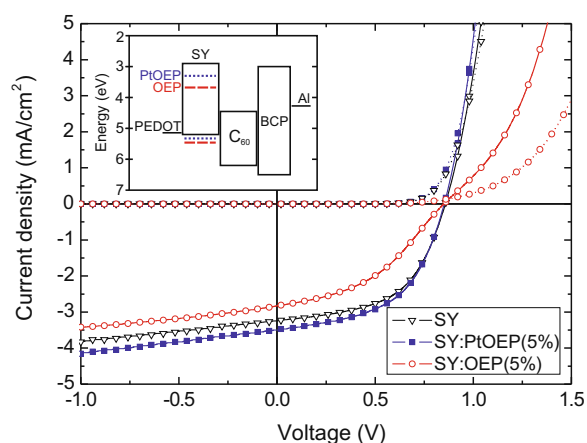


Fig. 2. Current density vs. voltage characteristics in the dark (dotted lines) and under 100 mW/cm² AM1.5D solar illumination (solid lines) with the following device structure: ITO/PEDOT (30 nm)/donor layer (15 nm)/C₆₀ (30 nm)/BCP (8 nm)/Al (80 nm). The donor layer is either pure SY (open black triangles), SY:PtOEP(5%) (filled blue squares), or SY:OEP(5%) (open red circles). Inset: schematic energy diagram of the device structure.

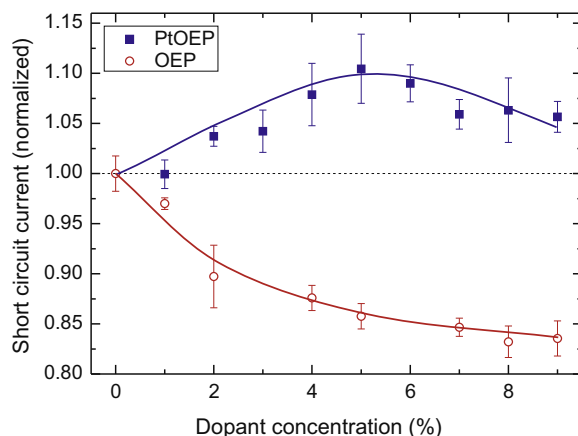


Fig. 3. The normalized short circuit current density vs. dopant concentration for the device structure of Fig. 2 with either PtOEP (filled squares) or OEP (open circles) as the dopant. The data points are representative of the average value of six devices while the error bar indicates the standard deviation. The lines serve as guides to the eye.

atomic force microscopy of doped (8%) and undoped SY films have smooth surface morphologies with root mean square roughnesses of 0.6 nm (data not shown). With an increase in PtOEP concentration, J_{SC} increases by approximately 10%, peaking at a dopant concentration of 5%, beyond which the increase in J_{SC} is reduced. In contrast, the addition of OEP to the SY matrix always results in a decrease of J_{SC} , which appears to saturate at a reduction of approximately 15–18%. This can be understood by considering again the results of Fig. 1, where SY singlets are immediately quenched by the addition of small amounts of the dopant. Once a sufficient doping level has been reached in order to quench a large percentage of the SY excitons, increasing the dopant concentration only suppresses further the transport of charges and/or triplet excitons in the SY layer, resulting in a decreased performance and therefore the presence of an optimal PtOEP concentration. Indeed, the fact that both dopants efficiently quench SY excitons but only PtOEP doping leads to an enhancement of J_{SC} provides significant evidence that excitons are returned to SY in that case, whereas with OEP doping they are lost.

As further evidence of the sensitized phosphorescence mechanism, we consider the external quantum efficiency (η_{EQE}) spectra of doped and undoped devices, as shown in Fig. 4a. To highlight the relative contributions from SY and C_{60} , we also show the calculated absorption efficiency (η_A) spectra for SY and C_{60} (using a transfer-matrix based calculation). The SY contribution is centered at $\lambda = 455$ nm, whereas C_{60} is responsible for the shoulder at $\lambda = 435$ nm and the tail extending to $\lambda = 650$ nm. The reduction of η_{EQE} at $\lambda \leq 375$ nm is due to reflection and absorption from the glass/ITO substrate, resulting in a “false peak” in the measured η_{EQE} at $\lambda = 375$ nm. The η_{EQE} spectrum of the cell with a pure SY donor layer shows distinct features of both SY and C_{60} . From η_A , it is clear that there is a larger contribution to the photocurrent originating from the C_{60} acceptor layer compared to that of SY,

which contributes approximately 15% of the total current, and which is consistent with the fact that OEP doping results in a reduction of J_{SC} by approximately the same amount (cf. Fig. 3). The calculated η_{EQE} spectrum for the undoped device closely fits that of the measured data, and yields an estimate of $L_D = 4 \pm 1$ nm, in excellent agreement to that of other PPV derivatives [22]. For the device with a SY:OEP(5%) donor layer, the contribution from SY is barely visible, functioning instead almost completely on C_{60} . Indeed, spectral fitting for this device requires $L_D \approx 1$ nm, indicating that only SY excitons formed at the interface with C_{60} are able to contribute. This is consistent with the fact that OEP quenches most SY excitons and confines them to the OEP dopant (where emission is observed, cf. Fig. 1b), eliminating the opportunity to dissociate at the donor–acceptor interface.

The η_{EQE} spectrum of the SY:PtOEP(5%) shows instead an enhancement of the SY signal, peaking at $\lambda = 450$ nm to $\eta_{EQE} = 45\%$. Here, SY contributes approximately 21% of the total current, an increase of about 40% compared to the undoped SY donor layer. In this case, L_D of SY triplet excitons is longer than that of singlet excitons, and therefore a larger percentage of photons absorbed in the SY layer are able to contribute to photocurrent. We are again able to obtain an excellent spectral fit, and this provides an estimate of $L_D = 9 \pm 1$ nm, significantly greater than that of the pure SY film. Indeed, the reported fluorescence lifetime of SY is 400 ps [23], whereas the triplet lifetime has been estimated from delayed fluorescence to be 5.6 ms [17], and therefore an increase in L_D could be expected. If we take the difference between η_{EQE} of doped and undoped devices, we obtain the curves as shown in Fig. 4b. Here the difference between the PtOEP-doped and pure SY devices is a result of increased signal from SY, as well as small contributions from PtOEP at $\lambda = 385$ and 535 nm. These contributions from PtOEP provide further evidence of the triplet transfer process, as direct absorption of PtOEP generates triplet excitons which

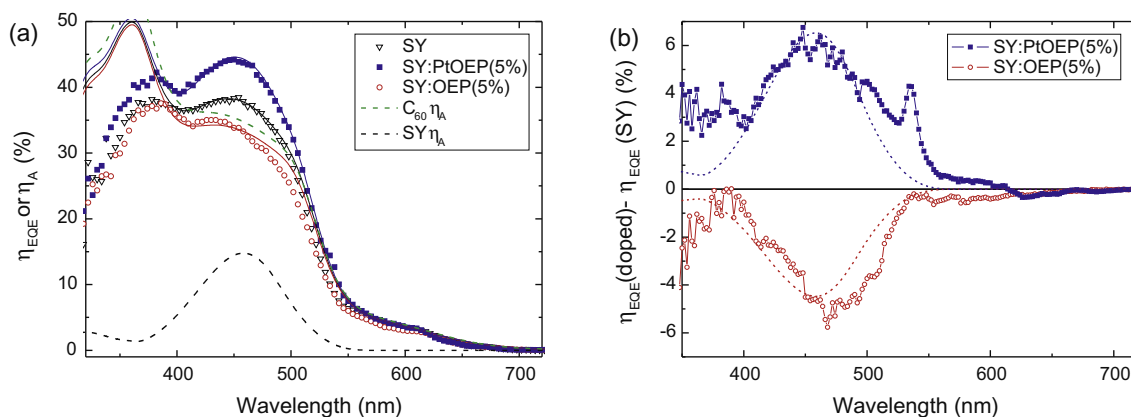


Fig. 4. (a) Measured external quantum efficiency (η_{EQE}) spectra for the device structures of Fig. 2 with donor layers of pure SY (open black triangles), SY:PtOEP(5%) (filled blue squares), or SY:OEP(5%) (open red circles). The solid lines show the calculated η_{EQE} spectra, with colors corresponding to that of the data points. The dashed lines show the calculated absorption efficiencies (η_A) of the SY (black) and C_{60} (green) layers within the device structure. (b) The difference in η_{EQE} between devices with doped and pure SY donor layers. The blue line with solid squares shows the device with PtOEP doping, and the red line with open circles shows the device with OEP as a dopant. The dotted lines represent the differences in the fits shown in (a). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

transfer to SY and are transported to the donor–acceptor interface, contributing to photocurrent. By contrast, the difference between the OEP-doped device and pure SY is negative and corresponds to a loss in the SY spectral response. Also in this spectrum, no additional contribution from the OEP dopant is observed, as would be expected for these immobile singlet excitons.

In conclusion, we have experimentally demonstrated an organic solar cell with a donor layer enhanced by the process of sensitized phosphorescence. By converting optically excited singlet excitons to triplet excitons efficiently, L_D was more than doubled, from 4 ± 1 to 9 ± 1 nm, which in turn increased the signal from this layer by 40%. In contrast, a similar dopant which lacks the ability to convert host singlet excitons to triplet excitons was shown to reduce the photocurrent from the host material. The ability to increase L_D , ideally toward distances equal to the absorption length in organic materials will allow simplified bilayer architectures to possess efficiencies approaching that of BHJ devices, or will at least relax the restrictions placed on the phase separation of blends. The design rules and methodology demonstrated here should lead to the development of new materials with suitable mobility and absorption spectra in order to optimize sensitized phosphorescent organic solar cells.

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