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Enhancement of photovoltaic efficiency of phosphor doped organic solar cell by energy and electron transfer from the phosphor to C₆₀ acceptor

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About 67% increase in power conversion efficiency (PCE) of copper phthalocyanine/C₆₀ based organic solar cells was demonstrated by doping 4 wt % iridium(III)bis(3-(2-benzothiazolyl)-7-(diethylamino)-2H-1-benzopyran-2-onato-N',C⁴)(acetyl acetonate) (IrC₆) into C₆₀ acceptor layer. The raised PCE was proved to result from the efficient photo absorption of IrC₆ followed by the energy and electron transfer from IrC₆ to C₆₀ due to the matched energy level alignment between these two species. Besides, IrC₆ could also increase the exciton dissociation efficiency at the active interface of the solar cells. The more detail improvement mechanisms were also discussed. © 2011 American Institute of Physics. [doi:10.1063/1.3658875]

Recently, the power conversion efficiency (PCE) of organic photovoltaic (PV) solar cells has been rapidly improved, which offered potential applications of low-cost renewable energy source. It is mainly due to the development of materials, device architectures, and processing techniques.^{1–6} For an organic material, the absorption of photons results in the creation of bound electron-hole pairs, i.e., excitons. When the excitons diffuse to a donor-acceptor (D-A) interface, they could be dissociated into free charge carriers, i.e., holes and electrons. Finally, the holes and electrons are collected by anode and cathode, respectively.

Long exciton diffusion length (L_D), high light absorption efficiency, efficient energy transfer, and exciton disassociation are crucial for achieving high PCE of PV solar cells. Generally, the exciton diffusion length (L_D) of fluorescent material in a PV diode is short, i.e., in the range of 3–10 nm. As a result, some photogenerated excitons would be recombined during the diffusing process before reaching the D-A interface.^{7,8} Long lifetime triplet excitons can be obtained by using phosphorescent material uniform layer or doping phosphor into the fluorescent active layer. In such a case, device efficiency could be enhanced by using thicker active layer and long-lived triplet excitons. On the other hand, doping phosphor into the active layer may also increase the absorption efficiency of the devices. Wade *et al.* have doped a phosphor *fac*-tris(2-phenylpyridine) iridium as a sensitizer into the PV device to enhance the L_D .⁹ Chan *et al.*^{10,11} have demonstrated improved PCE in their solar cells by doping fluorescent dye rubrene into the active layers.

In this work, we demonstrated enhanced efficiency of Ir-complex phosphor doped organic PV solar cells with a structure of copper phthalocyanine (CuPc)/IrC₆ doped C₆₀/Bphen; here IrC₆ indicates iridium (III)bis(3-(2-benzothiazolyl)-7-

(diethylamino)-2H-1-benzopyran-2-onato-N',C⁴)(acetylacetonate) and Bphen is 4,7 diphenyl-1,10-phenanthroline. The IrC₆ has previously been used as a red phosphor emitter,¹² but it has not been used in PV solar cells. The PCE of the PV device doped with 4 wt. % IrC₆ was enhanced by 65%. The improvement is attributed to the effective energy and electron transfer, enhanced light absorption, and efficient exciton dissociation.

All PV devices were fabricated on pre-cleaned indium-tin-oxide (ITO) glass with a sheet resistance of 25 Ω /sq. The substrates were UV ozone treated immediately before the device fabrication. The deposition rates of organic and Al layers were controlled to 2 \AA /s and 10 \AA /s by vacuum evaporation at a pressure of about 10^{-7} Torr, respectively. All organic materials were purified by sublimating for twice before used. Organic films were deposited on quartz substrates for the absorption spectra measurement with a Shimadzu UV-3101PC spectrophotometer. Current-voltage (J-V) characteristics were measured using Keithley-2400 under AM1.5 solar illuminations with an Oriel 150 W solar simulator. The singlet (S_1) and triplet energy (T_1) levels of CuPc, C₆₀ and 4-(dicyanomethylene)-2-*t*-butyl-6-(1,1,7,7-tetramethyl-julolidyl-9-enyl)4H-pyran (DCJTB) were cited from literatures, respectively.^{12–14}

In order to optimize the IrC₆ doping content in C₆₀ acceptor, 0, 1, 2, 4, and 8 wt. % IrC₆ were used, respectively. Note that 4 wt. % IrC₆ doped PV cell presents the maximum photocurrent response. To elucidate the mechanisms of the enhanced PV response by adding 4 wt. % IrC₆, a red fluorescent DCJTB doped device was also fabricated for comparison because DCJTB has a similar absorption spectrum with IrC₆ between 400–500 nm.^{13,14} Three PV devices were fabricated with structures as follows:

Device-C₆₀: ITO/CuPc (20 nm)/C₆₀ (40 nm)/Bphen (10 nm)/Al (200 nm);

Device-DCJTB: ITO/CuPc (20 nm)/C₆₀: 4 wt. %DCJTB (40 nm)/Bphen (10 nm)/Al (200 nm);

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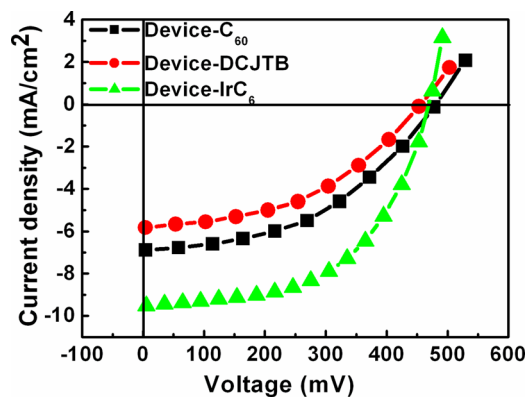


FIG. 1. (Color online) J-V characteristics of Device- C_{60} , Device-DCJTb, and Device- IrC_6 .

Device- IrC_6 : ITO/CuPc (20 nm)/ C_{60} : 4 wt. % IrC_6 (40 nm)/Bphen (10 nm)/Al (200 nm).

Figure 1 depicts the J-V characteristics of Device- C_{60} , Device-DCJTb, and Device- IrC_6 . Table I lists the performance parameters of the three devices extracted from their J-V characteristics, respectively. The results show that an increase in photocurrent density of Device- IrC_6 is observed compared to that of Device- C_{60} and Device-DCJTb. The short-circuit current density (J_{SC}) of Device- IrC_6 is 9.5 mA/cm², which is increased by 2.6 mA/cm² compared to Device- C_{60} .

Figure 2 displays the absorption spectra of the C_{60} : C_{60} : DCJTb (4 wt. %), and C_{60} : IrC_6 (4 wt. %) films, and the spectra were normalized at 266 nm. The absorption of C_{60} is assigned to electronic transitions of $\pi \rightarrow \pi^*$ lying at 250–400 nm and $\pi \rightarrow \pi^*$ lying at 400–700 nm, respectively,⁸ and the latter absorption is obviously lower than that of the former. A stronger absorption of IrC_6 lying at 400–500 nm region is mainly assigned to electronic transition from the ground state (S_0) to ¹MLCT and to ³MLCT due to the charge transfer from the metal to ligand, here ¹MLCT and ³MLCT denote the excited singlet and triplet states, respectively. Furthermore, the absorption spectrum of C_{60} : IrC_6 film matches better than C_{60} film with the standard solar spectrum.¹⁵ Thus, the additional absorption of C_{60} : IrC_6 film could directly contribute to the PV response.

On the other hand, energy transfer plays another important role in PV devices. The excited state levels of the C_{60} , DCJTb, and IrC_6 , as well as the possible energy transfer processes in the PV devices are described in the inset of Fig. 3. Under illumination, singlet excitons are formed in C_{60} and IrC_6 molecules, and then, they are converted to their triplet states by very fast intersystem crossing (ISC), respectively. The singlet excitons of C_{60} would be converted to longer-lived triplet excitons with a high rate driven by an

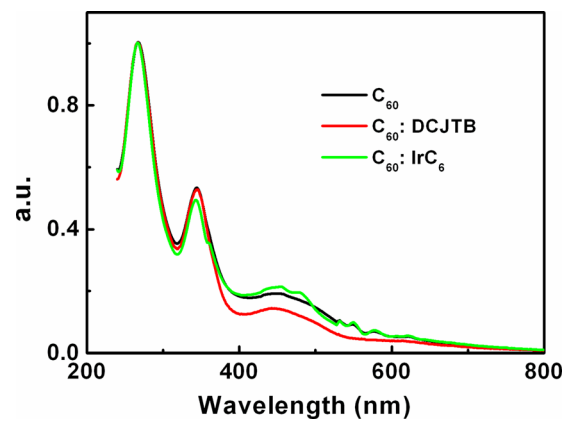


FIG. 2. (Color online) The absorption spectra of various films: neat C_{60} film, blend films of C_{60} : DCJTb, and C_{60} : IrC_6 (normalized at 266 nm).

efficient spin-orbit coupling.^{16,17} Moreover, both the S_1 and T_1 of IrC_6 are higher than the S_1 of C_{60} .¹⁸ Such a matched energy level alignment would lead to energy transfer from IrC_6 to C_{60} . For Device-DCJTb, only the singlet excitons were harvested and the DCJTb S_1 is markedly lower than the S_1 and T_1 of C_{60} , indicating that the energy transfer from C_{60} to DCJTb could take place. The L_D of DCJTb singlet exciton is shorter than that of C_{60} triplet singlet exciton. As a result, the PCE of Device-DCJTb was decreased.

The decay times of the neat IrC_6 and 4 wt. % C_{60} doped IrC_6 films are indicated in Fig. 3. We found that the excited state lifetime of IrC_6 molecules decreased from 2.57 to 0.38 μ s due to 4 wt. % C_{60} doping. The decrease of the decay time is probably the result from the energy and/or electron transfer from IrC_6 to C_{60} .¹² So, experiments were made to confirm the carrier transfer in C_{60} and dopant blend film, here the dopant is DCJTb and IrC_6 , respectively. Two devices were fabricated as follows:

Device-DCJTb/ C_{60} : ITO/DCJTb (10 nm)/ C_{60} (30 nm)/Bphen (10 nm)/Al

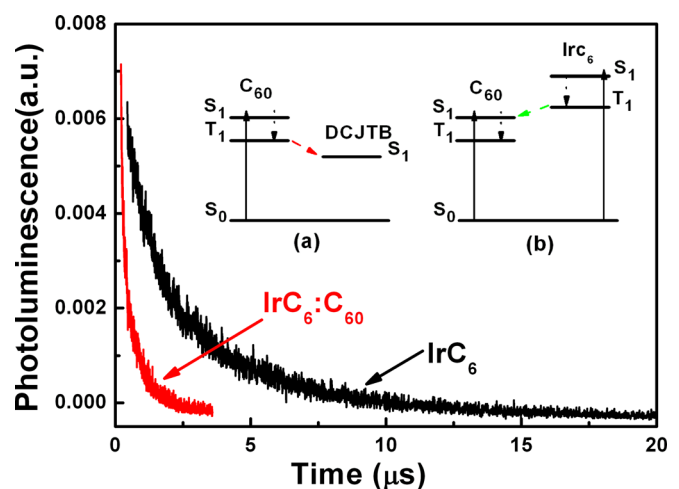


FIG. 3. (Color online) The time-resolved phosphorescence signals of IrC_6 and 4 wt. % C_{60} doped IrC_6 films, the decay times are indicated in the figures. Inset: the excited state levels of the DCJTb, IrC_6 , and C_{60} molecules as well as the possible energy transfer processes. Solid line arrowhead: absorption, down-dot line arrowhead: ISC; Diagonal dash line arrowhead: energy transfer from T_1 to S_1 .

TABLE I. The PV parameter comparison between of Devices- C_{60} , -DCJTb, and - IrC_6 . (V_{OC} : open-circuit voltage and FF : fill factor).

Device	J_{SC} (mA/cm ²)	V_{OC} (V)	FF	PCE(%)
Device- C_{60}	6.9	0.49	0.44	1.5
Device-DCJTb	5.8	0.46	0.44	1.2
Device- IrC_6	9.5	0.46	0.55	2.4

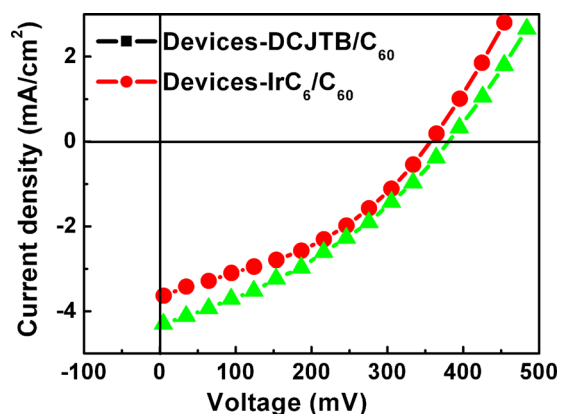


FIG. 4. (Color online) J-V characteristics of Device-DCJTb/C₆₀ and Device-IrC₆/C₆₀.

Device-IrC₆/C₆₀: ITO/IrC₆ (10 nm)/C₆₀ (30 nm)/Bphen (10 nm)/Al.

Figure 4 indicates the J-V characteristics of Device-DCJTb/C₆₀ and Device-IrC₆/C₆₀. It can be seen that Device-IrC₆/C₆₀ also offers a higher photocurrent response than Device-DCJTb/C₆₀, indicating that the exciton could also be efficiently dissociated at IrC₆/C₆₀ interface and the IrC₆ layer can also act as a hole transport layer. In order to prove that the additional PV response does not come from contribution of Bphen layer, the ITO/C₆₀ (40 nm)/Bphen (10 nm)/Al device was also fabricated. The photocurrent response of C₆₀/Bphen device can be neglected compared with that of Device-IrC₆/C₆₀. In addition, in Device-IrC₆/C₆₀, IrC₆ directly connects with the anode, there is not any other material to transport hole, so we can conclude that photogenerated hole can also be transported by IrC₆. This result indicates that IrC₆ doped C₆₀ could also promote exciton dissociation, that is, IrC₆ could transport charge carrier in the IrC₆:C₆₀ blend film at a certain extent, which could contribute to the improvement in PCE.

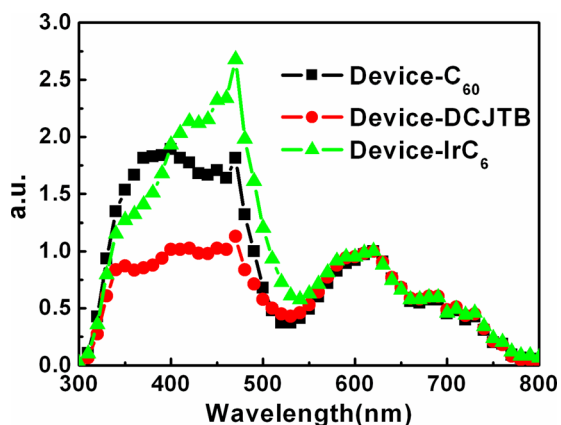


FIG. 5. (Color online) Photocurrent response curves of Device-C₆₀, Device-DCJTb, and Device-IrC₆.

Figure 5 depicts the photocurrent response curves of Device-C₆₀, Device-DCJTb, and Device-IrC₆. It is shown that the photocurrent of Device-IrC₆ is higher than Device-C₆₀ between 400 to 530 nm, which matches the absorption of IrC₆:C₆₀. However, the photocurrent of Device-DCJTb is declined between 350 nm to 470 nm, which is corresponding to C₆₀ absorption waveband. This phenomenon implies that C₆₀ exciton is not dissociated into carriers, in contrast its energy is transferred to DCJTb with short L_D due to the lower energy level.

In summary, we demonstrated a PCE enhancement by over 67% for organic PV solar cell with a structure of ITO/CuPc/C₆₀: IrC₆ (4 wt. %)/Bphen/Al. The increase in PCE was mainly attributed to the mechanisms: IrC₆ could transfer its energy to C₆₀ acceptor and IrC₆ could also increase both the light absorption and exciton dissociation efficiency of the PV solar cell. Furthermore, the long L_D of IrC₆ is also an important factor. The findings indicate that organic phosphors with long lifetime and suitable energy level can be doped into organic active layers for increasing the PCE of organic PV solar cells.

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