# Exploring photocurrent output from donor/acceptor bulk-heterojunctions by monitoring exciton quenching*

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In this work, a series of polymer bulk-heterojunctions is fabricated based on the combinations of different donors (Ds) (P3HT and PCPDTBT) and acceptors (As) (PCBM, ICBA, and F8BT). Exciton quenching efficiencies of the D–A pairs are obtained in order to quantify charge-transfer between the donor and the acceptor via a modified approach developed in conjunction with experimental results of optical absorption and photoluminescence spectra. It is discovered that the exciton quenching efficiency in the combination of PCPDTBT:PCBM and P3HT:PCBM reaches 70% and over, but in PCPDTBT:ICBA it is about 12%. A relatively high $\Delta \mathrm{LUMO}_{\mathrm{donor-acceptor}}$ results in a relatively high exciton quenching efficiency, which is responsible for better charge separation. The results agreed well with the photocurrent effect of the heterojunction layers. The work offers a convenient way to predict a potentially promising photovoltaic material with a selected D–A pair.

**Keywords:** exciton quenching, optical absorption, photoluminescence, photocurrent

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## 1. Introduction

Polymer solar cells have advantages in low-cost fabrication, flexibility, light weight, and a wide range of material selections, which form a promising option in solar energy applications. Recent investigation revealed that the cell structure can be optimized in order to improve efficiency via thermal annealing,[1–3] selection of solvents or solvent combination,[4,5] tuning the band gap of the polymers,[6] modified electrode,[7] etc. These will affect the photoelectric conversion efficiency of the photovoltaic device by modifying their light absorption, transmission or refraction, exciton generation, diffusion, separation and combination, charge–transfer (CT) process, as well as carrier transport of active layers. A considerable amount of research effort in the past has been devoted to the analysis of the above processes in order to explore the loss mechanism in the power conversion, which appears to be a barrier hindering the commercialization of polymer solar cells.

It has been proposed that the nature of a donor (D)–acceptor (A) pair and the match of their energy levels play an important role in exciton generation, dissociation, and CT processes in an organic photovoltaic device, which in turn have a strong influence on the device performances.[8] The mechanism to generate free carriers from radiation-excited exciton generation in organic solar cells is the most controversial issue. Broadly speaking, the donor and/or acceptor in an active layer absorb photons and generate excitons. The excitons migrate to the D/A interface to allow the electron transfer to the acceptor or donor (an exciton transfer process).[9–12] The exciton is then dissociated at the interface into electron and hole, a key step that determines the output current and hence the photoelectric conversion efficiency of the cells.[13,14] Transferring electrons from a donor to an acceptor is called the CT process. However, only the exciton which is dissociated into the free charge carriers will contribute to the photocurrent. The knowledge of the CT process is useful in understanding the mechanism regarding photocurrent generation.

In a photoexcitation dynamics investigation, Piris *et al.* related the role of [6,6]-phenyl-C61 butyric acid methyl ester (PCBM) in poly(3-hexylthiophene)(P3HT)/PCBM blends with the charge separation and collection, and proposed three possible processes which might be encountered in the charge-transfer:[15] (i) photoexcited ultrafast ($< 200$ fs) electron transfer from donor to nearby acceptor; (ii) electron transfer induced photo-generated electron–hole pairs in the donor; and (iii) exciton diffusion to the interfaces of donor and acceptor followed by an electron transfer to the acceptor. It can be noticed that all three cases quench the exciton in donor P3HT. It is therefore possible to relate the exciton quenching process with the exciton dissociation and free carrier generation. The electrons transferred may be divided into two categories: the bound charges, and the free charges.[8,16] The former are still associated with the hole in the donor via Coulomb interaction

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(not free) and remain in a CT state.[17] The formation of the free carriers needs to separate the exciton further.

The exciton quenching in a D/A structure can be detected using transient approaches, such as, transient absorption spectrum[15,16,18,19] and light-induced electron spin resonance spectrum,[19,20] or steady-state methods, e.g. light-induced absorption[20] and absorption-detected magnetic resonance spectrum.[21] Among these, the transient absorption spectrum is able to provide quantitative or qualitative analysis about the energy transfer process, through a time-resolved spectrum of stimulating samples in a certain frequency domain. In this approach, a sample is first illuminated with a broadband light pulse that is used to determine the ground-state spectrum of the sample. This is followed by a short pulse of a wavelength strongly absorbed by the sample to create excited states, and a second broadband pulse probes the transmission spectrum of the excited sample.[22] This offers an important means for the in-depth studying of the exciton dissociation and the CT mechanism. Charge photogeneration in organic donor/acceptor blend film studied by ultrafast transient optics was first reported by Brabec *et al*.[23] In Refs. [9], [23], and [24] the charge generation in MDMO-PPV:PCBM blend film was found to occur within $< 100$ fs. Nevertheless, this technique is considered to be capable of distinguishing between CT states and fully dissociated polarons.[9] However, all these methods require the use of sophisticated instruments. Hence only limited investigation was reported.

If the CT process is accompanied with an exciton quenching process, it offers a chance to detect the CT by a steady-state means in combination with absorption and photoluminescence, which is substantially simplified in comparison to the transient methods and provides more quantitative information than the other steady-state methods. An exciton quenching efficiency is involved in electrons transferring from donor to acceptor (the first step of the formation of CT states or fully dissociated polarons), which was evaluated by Pierre *et al*. recently by using a combination of absorption and photoluminescence (PL) spectra.[25] This presented an easy access to the evaluation of the exciton quenching efficiency by using conventional analytic instruments. In our present work, a modified approach is proposed to improve analysis accuracy through using absorption-weighted PL emission by taking account of the difference in absorption co-efficiency between the materials when it determines the maximum of light emission from a mixture.

In this work, a series of polymer bulk-heterojunction testing devices using a set of four donor (polymers) and acceptor pairs is fabricated and investigated. Photocurrent responses of the devices are compared with the exciton quenching efficiencies measured. It is found that the latter is correlated well with the device performance. It offers a useful tool to predict a suitable device structure for cell engineering.

## 2. Experiment

### 2.1. Materials and the preparation of thin film devices

The materials used in this work include the following donors: P3HT (purity 98.5%) and poly[2,6-(4,4-bis-(2-ethylhexyl)-4H–cyclopenta-[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)](PCPDTBT) (purity 99%); and acceptons: PCBM (purity 99%), indene-C60 bisadduct (ICBA) (purity 99%) and poly(9,9-dioctylfluorene-co-benzothiadiazole) (F8BT) (purity 99%) as shown in Fig. 1, which were purchased from Taiwan Luminescence Technology Corp. Electrode or buffer materials poly(3,4-ethylenedioxy-thiophene):poly(styrenesulfonate)(PEDOT:PSS)(PVp. A14083) were purchased from Heraeus Co. (German) and Al (purity $> 99.9\%$) was purchased from Beijing General Research Institute of Nonferrous Metals. LiF (purity $> 99.7\%$) or chemicals or solvents not specified were purchased from Beijing Chemical Reagent Company. Conductive indium-tin-oxide (ITO) glass substrates (10 Ω/□) were purchased from CSG Holding Co., China.

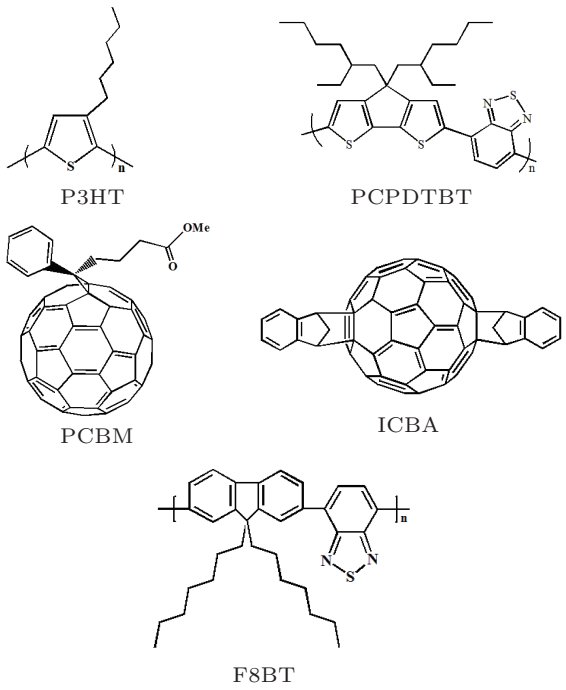



**Fig. 1.** Chemical structural formulas of P3HT, PCPDTBT, PCBM, ICBA, and F8BT.

Donors and acceptors were dissolved in an ortho-dichlorobenzene solvent first. Thin films were prepared by spin coating from pristine materials or D/A blends (PCPDTBT:PCBM, PCPDTBT:ICBA, P3HT:PCBM, and P3HT:F8BT), in which the blends have a mass ratio of 1:1 on quartz substrates in order to ensure the accuracy and repeatability of the experiment. Different film thickness values were controlled by adjusting spinning rates or concentrations. These films were used in absorption and photoluminescent measurements.

Polymer bulk-heterojunction photovoltaic devices were fabricated with a general structure of ITO/PEDOT:PSS/active layer/LiF/Al. The ITO substrates were cleaned in an ultrasonic bath with deionized water, acetone, ethanol, acetone, and ethanol, for 20-min each respectively. Then they were transferred into an ozone chamber to treat further for 7 min. PEDOT:PSS was then spin-coated onto the ITO substrates at 3000 rpm for 40 s and annealed at 120 °C for 15 min in the air. To avoid oxygen and moisture, the substrates were transferred into a nitrogen-filled glove-box, where the active layers were spin-coated from ortho-dichlorobenzene solutions. Buffer layer LiF (1 nm) and Al electrode (80 nm) were vacuum deposited using a thermal vacuum evaporation coating machine (Beijing Technol. Science Co.). Film thicknesses were finally measured using a surface profiler (US Ambios Technology co, XP-2).

### 2.2. Characterization and device testing

Absorption spectra of the materials were measured by an ultraviolet-visible (UV-Vis) spectrophotometer (Shimadzu, UV-310IPC). Photoluminescence spectra were obtained from a combined measurement system for infrared fluorescence (Nanolog FluoroLog-3-2-iHR 320). *J*–*V* characteristics of the devices was taken with a source measurement unit (Keithley 4200). A solar simulator (Abet, SUN 2000) was used for the measurement of solar cells under a standard condition [AM1.5, 1 kW·m$^{-2}$] and ambient environment.

## 3. Results and discussion

### 3.1. Photophysical properties of the donor/acceptor pairs

UV-Vis absorption and photoluminescence (PL) properties of a series of donors and acceptors are investigated from a pristine donor, the acceptor and D/A blends (PCPDTBT:PCBM, PCPDTBT:ICBA, P3HT:PCBM, and P3HT:F8BT) are measured. The results are shown in Figs. 2 and 3 respectively.

Taking a combination of pristine donor PCPDTBT, acceptor ICBA, and their blend for example, it is found that PCPDTBT is absorbed strongly in the UV-Vis spectral range, and has two broad absorption peaks around 410 nm and 700 nm, while ICBA is absorbed differently and is located in the short wavelength range. The blend of PCPDTBT:ICBA demonstrates an additive spectrum of PCPDTBT and ICBA, similar to that of the PCPDTBT component. The values of absorption coefficient ($\alpha$) of the materials are calculated from the absorption spectra and the thickness values of the films. The absorption coefficients of PCPDTBT and ICBA are estimated at 475 nm, to be 0.8 μm$^{-1}$ and 2.1 μm$^{-1}$, respectively (see Table 1). The highest occupied molecular orbital (HOMO) levels and the lowest unoccupied molecular orbital (LUMO) levels of the donors and acceptors are cited from the relevant literature, and are also listed in Table 1 for comparison.

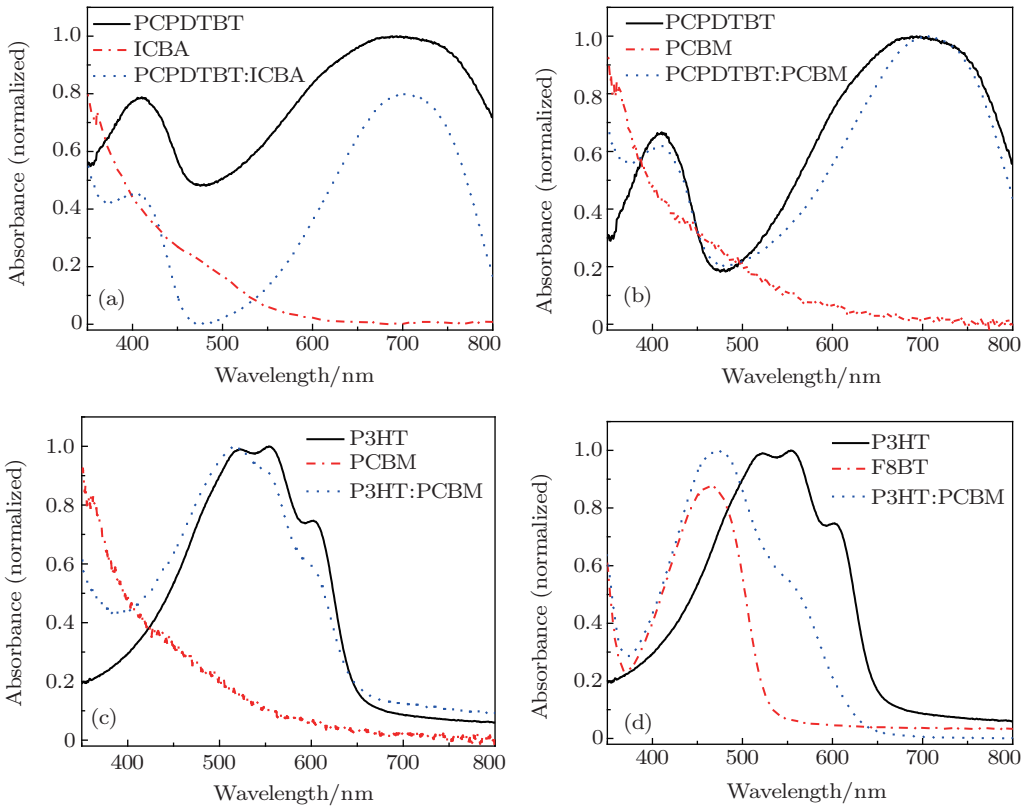



**Fig. 2.** (color online) Absorption spectra from D/A blended films as indicated.

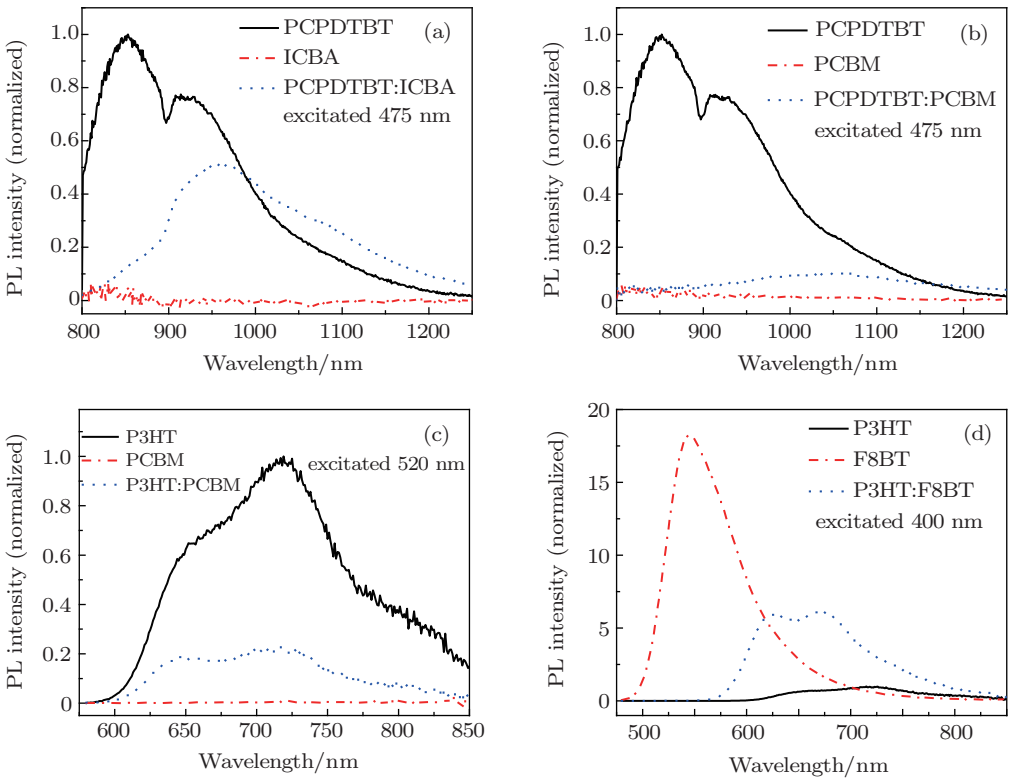



**Fig. 3.** (color online) PL spectra from D/A blended films as indicated.

**Table 1.** Absorption peaks and coefficients, photoluminescence peaks, and the energy levels of pristine materials.

| Materials | Peak absorption/nm | $\alpha$/μm$^{-1}$ (at $\lambda_{EX}$) nm | PL/nm | HOMO/eV | LUMO/eV |
|---|---|---|---|---|---|
| PCPDTBT | 410, 700 | 0.8 (475) | 850, 935 | –4.9 | –3.5[26] |
| P3HT | 520, 555, 600 | 7.5 (520) 1.9 (400) | ∼ 650, 720 | –5.1 | –3.2[26] |
| ICBA | < 350 | 2.1 (475) | – | –5.9 | –3.74[27] |
| PCBM | < 350 | 3.6 (475) | – | –6.1 | –4.3[26] |
| F8BT | 465 | 2.2 (400) | 545 | –5.74 | –3.3[28] |

$\alpha$: absorption coefficients; $\lambda_{EX}$: the excited wavelength.

The PL spectra of the pristine PCPDTBT, ICBA, and the PCPDTBT:ICBA blend are monitored when excited at a wavelength of 475 nm (see Fig. 3(a)). It can be observed that PCPDTBT is emitted near 850 nm (1.46 eV) with a shoulder around 935 nm (1.33 eV), but ICBA exhibits no emission within the spectral range 800 nm–1200 nm studied. However, when mixing both PCPDTBT and ICBA together into a blend, it is found that the acceptor ICBA quenches the PCPDTBT emission in the blend film and causes a considerable reduction in the PCPDTBT emission. At the same time, the PCPDTBT emission is red-shifted by about 0.18 eV from the pristine PCPDTBT emission, to around 960 nm (shifted by 1.29 eV) for the main peak, and to ∼ 1090 nm (shifted by ∼ 1.14 eV) for the long-wavelength shoulder. A moderate red-shift in PL emission of PCPDTBT in the blend indicates an interaction between the donor and acceptor, which lowers the energy in the excited state of the donor PCPDTBT$^*$.

Three more combinations of the donor/acceptor pairs (PCPDTBT:PCBM, P3HT:PCBM, P3HT:F8BT) are also investigated. The UV-Vis absorptions and the PL emissions from the pristine P3HT, PCPDTBT, PCBM, F8BT and the blends are also presented in Figs. 2 and 3, and the data are listed in Table 1. PL spectra are taken at different excitation conditions to adapt their individual absorptions: i.e., 475 nm for the PCPDTBT/PCBM pair; 520 nm for the P3HT/PCBM pair; and 400 nm for P3HT/F8BT pair as shown in Fig. 3 and their emission peaks are also listed in Table 2.

As for PCPDTBT:PCBM blend, it can be seen that the UV-Vis absorption spectrum from the blend is very similar to that of PCPDTBT:ICBA blend: i.e., it is again an additive spectrum of the two components (PCPDTBT and PCBM). However, the acceptor PCBM quenches the emission from PCPDTBT in PCPDTBT:PCBM blend much more effectively than that in the PCPDTBT:ICBA blend. Only a residual emission of PCPDTBT remains in the blend. Again the multiple emission from PCPDTBT is red-shifted by about 0.26 eV

from the pristine PCPDTBT emission. The moderate shift indicates a slightly lowered energy in the excited state of the donor PCPDTBT* in the PCPDTBT:PCBM blend, owing to the interaction, but at a slightly higher degree than that in the PCPDTBT:ICBA blend.

In the P3HT/PCBM combination, a similar effect is observed. The absorption spectra of the blend are similar to the additive spectra of the pristine P3HT and PCBM. Also severe quenching of the donor emission of P3HT occurs in the P3HT:PCBM blend. The multiple emission from P3HT in the blend is blue-shifted slightly by about 0.01 eV from the pristine P3HT emission. As the shift is so small, the energy level change, as a result of the interaction between the donor and acceptor, may be ignored.

**Table 2.** Values of exciton quenching efficiency calculated with and without absorption coefficients, peak absorption, PL, PL shift, $\Delta LUMO_{donor-acceptor}$ of D/A and the $J_{SC}$, $V_{OC}$ of devices.

| Materials | Peak absorption/nm | PL/nm | PL shift/eV | $\eta_{donor}$ [a] (this method) | $\eta_{donor}$ [b] (Ref. [20] method) | $J_{SC}$/(mA/cm$^2$) | $V_{OC}$/V | $\Delta LUMO_{D/A}$/eV |
|---|---|---|---|---|---|---|---|---|
| PCPDTBT:ICBA | 410, 700 | 960, 1090 | 0.18 | 0. 12 | 0. 52 | 2.11 | 0.90 | 0. 24 |
| PCPDTBT:PCBM | 410, 700 | 1045, 1150 | 0.26 | 0. 78 | 0. 90 | 2.85 | 0.71 | 0. 8 |
| P3HT:PCBM | 520, 555, 600 | 645, 715 | 0.01 | 0.74 | 0.84 | 6.23 | 0.61 | 1. 1 |
| P3HT:F8BT | 470, 555 | 620, 675 | 0.10 | 0.28 ($\eta_{acceptor}$) | 0.24 ($\eta_{acceptor}$) | $< 0.1$ | 0.82 | 0. 1 |

[a] Calculated from Eq. (1) in this work; [b] Calculated using Pierre's method in Ref. [25]. $\eta_{donor}$ or $\eta_{acceptor}$ is the exciton quenching efficiency of each D/A structure monitored donor or acceptor emission.

The P3HT/F8BT pair is a special one as they are both photoluminescent, where F8BT emits a single peak at 545 nm, and P3HT shows multiple emissions at around 650 nm and 720 nm (1.90 eV and 1.72 eV). However, the PL emission from the P3HT:F8BT blend is obviously multiple and similar to that of P3HT, with a considerable increase in intensity compared with that of the pristine P3HT. These emissions, however, are blue-shifted by about 0.10 eV from the pristine P3HT emission and located at 620 nm and 675 nm (2.00 eV and 1.84 eV) respectively. Emission from F8BT is completely lost in the blend, owing to energy transfer from F8BT to P3HT, since there exists an overlap between the emission of F8BT and the absorption of P3HT. Consequently, it results in a quench of the acceptor F8BT emission by the donor P3HT, via energy transfer from F8BT to P3HT, which is different from the previous three cases.

### 3.2. Exciton quenching efficiency, charge-transfer, and photocurrent of the devices

Spectroscopy can be a sensitive tool to monitor the interactions between the two components of the blend. For example, the change in absorption spectrum indicates a change in the ground-state molecular orbital or the formation of a molecular complex.[29] The PL emission change is associated with the change in the excited-state, as well as in the ground-state of the molecule to be studied. Simple quenching relating to the energy transfer between the two species only alters the intensity of the emission, whereas the interactions between the molecule and the quencher in the blend may result in a spectral variation as well, for example, the formation of exciplexes, excited-state CT complexes between the donor and acceptors.[30] In general the change of UV-Vis absorption and/or the PL emission of the blends, in comparison to their pristine donors or acceptors, can be used to monitor the interactions between the two components.

Exciton quenching efficiency ($\eta$) can be used to quantify the quenching process. For the first approximation, it can be estimated through the intensity variation of the PL spectrum from D/A blend, when compared with that from its pristine material. Assuming the absorption of the specimen and the PL of each donor or acceptor component are known, and there is no interaction between the donor and the acceptor, an ideal but hypothetical PL emission excited at $\lambda_{ex}$, $PL_{0,norm,\lambda ex}(\lambda)$, of a D/A blend may be obtained purely by adding the two spectra at a certain ratio, as expressed below

$$PL_{0,norm,\lambda_{EX}}(\lambda) = \frac{f_A\alpha_A}{f_A\alpha_A + f_D\alpha_D} \cdot \frac{PL_A(\lambda)}{1-10^{-OD_A}} + \frac{f_D\alpha_D}{f_A\alpha_A + f_D\alpha_D} \cdot \frac{PL_D(\lambda)}{1-10^{-OD_D}}\Bigg|_{\lambda_{EX}}, \quad (1)$$

where $PL_A(\lambda)$ and $PL_D(\lambda)$ are the PL spectra from the pristine acceptor and donor components; $OD_D$ and $OD_A$ are optical densities measured from the donor and acceptor, respectively; $\alpha_D$ and $\alpha_A$ represent the absorption coefficients of donor and acceptor, calculated from the absorption spectra and the film thicknesses; $f_D$ and $f_A$ are the fractions of the D and A components in the D/A blend. The term $PL_A(\lambda)/(1-10^{-OD_A})$ (or $PL_D(\lambda)/(1-10^{-OD_D})$) is a normalized PL by light absorption from an acceptor (or donor). It is a quantity related to PL quantum efficiency of A (or D). The fraction $f_A\alpha/(f_A\alpha + f_D\alpha)$ (or $f_D\alpha/(f_A\alpha + f_D\alpha)$) is an absorption-weighted fraction of the acceptor (or donor), and is taken as a correction factor to take account of the light absorption capability by each component, because only the fraction capable of absorbing light may contribute to the PL emission. Our method is therefore different from Pierre *et al.*'s, where

only a simple material fraction is considered.[25]

In practice, the PL spectrum of a D/A blend can be measured directly. The quantity, $\mathrm{PL}_{\mathrm{BHJ,norm},\lambda\mathrm{ex}}(\lambda)$, may also be expressed by using a similar normalized form as shown below

$$\mathrm{PL}_{\mathrm{BHJ,norm},\lambda_{\mathrm{ex}}}(\lambda) = \left.\frac{\mathrm{PL}_{\mathrm{BHJ}}}{1-10^{-OD_{\mathrm{BHJ}}}}\right|_{\lambda_{\mathrm{EX}}}, \tag{2}$$

which represents the PL quantum efficiency from a bulk-heterojunction blend when excited at $\lambda_{\mathrm{ex}}$. The difference between the measured $\mathrm{PL}_{\mathrm{BHJ,norm},\lambda\mathrm{ex}}(\lambda)$ and the hypothetical $\mathrm{PL}_{0,\mathrm{norm},\lambda\mathrm{ex}}(\lambda)$ reveals the quenching of the PL as a result of the mixture of the D and A in the blend. It is therefore used to estimate exciton quenching efficiency, $\eta_{\mathrm{D}}$, as expressed below

$$\eta_{\mathrm{D},\lambda_{\mathrm{ex}}} = \left.\frac{\int[\mathrm{PL}_{0,\mathrm{norm},}(\lambda)-\mathrm{PL}_{\mathrm{BHJ,norm}}(\lambda)]\,\mathrm{d}\lambda}{\int \mathrm{PL}_{0,\mathrm{norm}}(\lambda)\,\mathrm{d}\lambda}\right|_{\mathrm{ex}}. \tag{3}$$

If exciton quenching efficiency can be used to represent the charge-transfer between D–A pairs, the problem is now simplified into the measurements of absorption and photoluminescence spectra from pristine D and A films, as well as their D/A blend, which can be implemented easily in most conventional laboratories.

Exciton quenching efficiency of PCPDTBT ($\eta_{\mathrm{PCPDTBT}}$) in the PCPDTBT:ICBA structure is measured and analyzed following the above procedures. Using film specimens of PCPDTBT (76 nm) and ICBA (155 nm), the absorption coefficients $\alpha_{\mathrm{PCPDTBT}}$ for PCPDTBT and $\alpha_{\mathrm{ICBA}}$ for ICBA at 475 nm are obtained from their absorption spectra, and found to be 0.8 $\mu\mathrm{m}^{-1}$ and 2.1 $\mu\mathrm{m}^{-1}$, respectively. The wavelength 475 nm is the excitation wavelength in the PL measurement. The exciton quenching efficiency of PCPDTBT in PCPDTBT:ICBA structure can be calculated, i.e., $\eta_{\mathrm{PCPDTBT:ICBA}} = 0.12$. The calculation results are listed in Table 2.

Similarly, the exciton quenching efficiencies of the PCPDTBT in the PCPDTBT:PCBM structure, P3HT in P3HT:PCBM, and F8BT in the P3HT:F8BT structures are also measured and analyzed in the same way (see Table 2). According to the calculation, the D–A pairs investigated give rise to different exciton quenching efficiencies in different blends. A higher exciton quenching efficiency indicates a better chance for the charges to transfer from donors to acceptors, and therefore a better chance of charge separation.

The simple bulk-heterojunction photovoltaic devices are prepared and characterized in the present study. The device parameters are compared with the evaluated exciton quenching efficiency. The four devices have a general configuration of ITO/PEDOT:PSS/active layer/LiF/Al, fabricated under the same conditions. The active layers are the D/A bulk-heterojunction layers, that is, PCPDTBT:PCBM, PCPDTBT:ICBA, and P3HT:PCBM, P3HT:F8BT. *J*–*V* characteristics of the devices are measured as shown in Fig. 4 and Table 2.

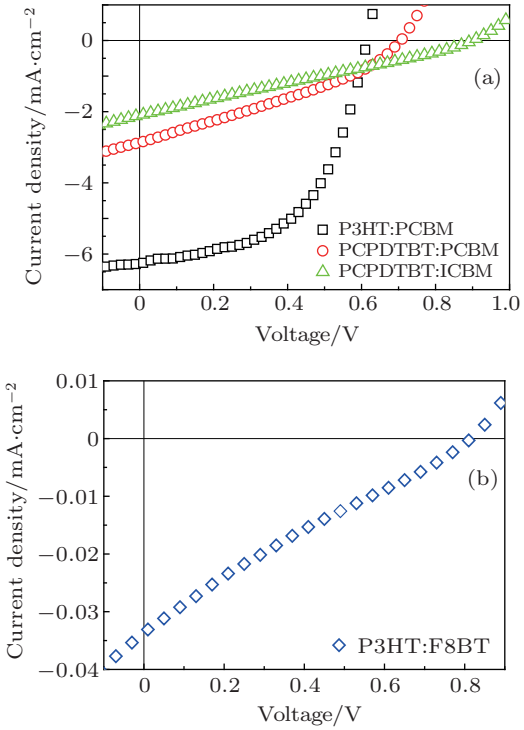



**Fig. 4.** (color online) *J*–*V* characteristics of the devices as indicated.

It can be seen from Fig. 4 that the values of short circuit current, $J_{\mathrm{SC}}$, of the devices are in the order of: $J_{\mathrm{SC(P3HT:PCBM)}} > J_{\mathrm{SC(PCPDTBT:PCBM)}} > J_{\mathrm{SC(PCPDTBT:ICBA)}} > J_{\mathrm{SC(P3HT:F8BT)}}$, while the order of the values of open circuit voltage, $V_{\mathrm{OC}}$, are almost reversed. A relatively high exciton quenching efficiency appears to give a higher $J_{\mathrm{SC}}$, except in the P3HT:F8BT case. As both PCBM and ICBA are not emissive, the quenching energy could lead to the charge separation. The more the excitons quenched, the higher the $J_{\mathrm{SC}}$ is. The result agrees with the calculated exciton quenching efficiency. In the P3HT-F8BT pair, however, the energy transfer from F8BT to P3HT forms a new exciton, which is responsible for the quenching of the F8BT emission. It does not therefore contribute to the charge separation and the $J_{\mathrm{SC}}$ becomes extremely low.

In order to understand device performances, the exciton quenching processes in these devices prepared by using different D–A pairs, are investigated and compared. It is believed that the degree of quenching may relate to the matching between energy levels of donor and acceptor.[28] It was suggested by Brédas that the exciton dissociation be related to an energy difference between the LUMO of a donor and the LUMO of an acceptor ($\Delta\mathrm{LUMO}_{\mathrm{D-A}}$). An energy difference of $\Delta\mathrm{LUMO}_{\mathrm{D-A}}$ less than 0.33 eV may be insufficient for an efficient exciton dissociation.[28] In order to analyze the devices in our present work, energy levels and the values of $\Delta\mathrm{LUMO}_{\mathrm{D-A}}$ of each D–A pair are also calculated in Table 2. The energy level diagrams are shown in Fig. 5. The values are cited from Refs. [26], [27], and [32]. In can be seen in these structures that the LUMO energy dif-

ference ($\Delta LUMO_{D-A}$) from device PCPDTBT:ICBA is 0.24 ($< 0.33$), which is insufficient to dissociate the exciton and the $\eta_{PCPDTBT:ICBA}$ is found to be very low ($\sim 0.12$). This explains the relatively low $J_{SC}$ in the device. In both P3HT:PCBM and PCPDTBT:PCBM devices, however, $\Delta LUMO_{D-A}$ are much higher than the required value 0.33. These are in excellent agreement with their exciton quenching efficiency values; i.e., $\eta_{P3HT:PCBM}$ in P3HT:PCBM blend is measured to be 0.74, and $\eta_{PCPDTBT:PCBM}$ in PCPDTBT:PCBM is measured to be 0.78. These indicate that there is an efficient exciton dissociation, hence there are relatively high $J_{SC}$ values in both the P3HT:PCBM device and the PCPDTBT: PCBM device.

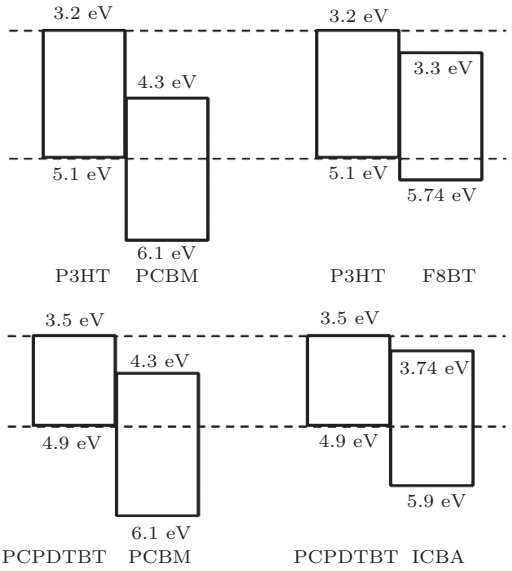



**Fig. 5.** Energy level diagrams of D–A pairs.

Another major difference among the four sets of devices is their spectral shift in PL emission. Emission from PCPDTBT is found to be moderately red-shifted in the blend either with ICBA or PCBM, which indicates the formation of exciplex by interacting the excited-state species of PCPDTBT. However, a slight blue-shift emission (0.01 eV) in P3HT with another acceptor may be caused by the polarity interaction between the species.

A comparative investigation into another D–A pair of P3HT:F8TBT was made by McNeill *et al.*[26] Although both F8BT and F8TBT are chemically similar, the P3HT:F8BT bulk-heterojunction solar cell was found to perform poorly in the blend with P3HT either in Ref. [33] or in this work. As P3HT:F8TBT blends can achieve reasonable efficient solar cell performance, despite an order of magnitude lower in electron mobility in blend with P3HT ($10^{-5}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ calculated from transistor characteristics)[34] than that in blend with F8BT ($10^{-3}$ $cm^2 \cdot V^{-1} \cdot s^{-1}$ by time-of-flight method),[33] it was argued that the electron mobility was not a key factor.[26] The origin of the poor efficiency of P3HT:F8BT blend deserves further investigation. In this work, it is found that the $J_{SC}$ in the P3HT:F8BT device is low as shown in Fig. 4(b), similar to those reported in Refs. [26] and [33]. Our investigation finds that it is the exciton energy transfer rather than the charge separation that occurs in the P3HT:F8BT blend. Furthermore the energy-transfer-caused light emission from P3HT is moderately blue-shifted (0.1 eV), which demonstrates a strong interaction between P3HT and F8BT as a result of lowering the ground-state energy of P3HT. This reduces the energy difference at the interface, and hence reduces the driving force for the charge separation. This is believed to be responsible for the poor photovoltaic response of the device. As a result, the energy transfer enhances the light emission from the P3HT component.

Investigation of the processes from CT states to free charge carriers has been a hot topic in the field of organic electronics. There is much research on this issue.[8,35] The present work offers a steady-state approach to evaluating the average transfer charges by using the exciton quenching efficiency as a quantitative parameter and offers a simple and convenient approach to screening suitable, promising D–A pairs for solar cell development.

## 4. Conclusions

In this work, a set of four D/A bulk-heterojunction polymer layers and the photovoltaic devices are fabricated. The exciton quenching process of the D–A pairs is investigated, where a modified approach is developed and used to calculate the exciton quenching efficiency, and to quantify the charge-transfer between the D–A combinations. The exciton quenching efficiency is found to be closely related to the $J_{SC}$ of the device. It is also strongly affected by the energy difference between the LUMO of the donor and the LUMO of the acceptor ($\Delta LUMO_{donor-acceptor}$). A relatively high $\Delta LUMO_{donor-acceptor}$ results in a relatively high exciton quenching efficiency, which is beneficial to the carrier separation. They are therefore responsible for a relatively high $J_{SC}$ in the devices of PCPDTBT:PCBM and P3HT:PCBM pairs. Similarly, the energy difference of $\Delta LUMO_{D-A}$ in the case of PCPDTBT:ICBA is too small for an efficient exciton dissociation. As a consequence, only a very low exciton quenching efficiency is detected, which explains the poor device performance. A different mechanism accounts for the P3HT:F8BT pair. Exciton energy transfer rather than charge separation occurs in the device. The strong interaction between P3HT and F8BT causes a strongly bonded exciton, which is hard to dissociate. This is responsible for the poor photocurrent action spectra of the device.

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