

Evidence of Harvesting Electricity by Exciton Recombination in an n–n Type Solar Cell

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Significant works,^{1–5} mainly on generating more free carriers from excitons, have been conducted since the first efficient donor–acceptor (D–A) type organic solar cell reported in the late 1980s.⁶ Up to now all organic solar cells,^{1–9} either small molecule- or polymer-based ones, are fabricated with a donor and an acceptor material to form a D–A interface, where the photogenerated excitons are dissociated for free carriers. Here we report a new n–n type heterojunction organic solar cell based on perfluorinated hexadecafluorophthalocyaninatozinc (F16ZnPc) and fullerene (C₆₀). Unlike the exciton dissociation in the existing D–A heterojunction organic solar cells, the recombination of excitons at the interface is used to produce free carriers. The recombination of electrons from F16ZnPc with holes from C₆₀ at the F16ZnPc–C₆₀ interface frees their counterpart carriers (electrons at C₆₀ side and holes at F16ZnPc side respectively), which are separated by a built-in electric field originated from the work function difference between the two electrodes and then collected by two electrodes to generate the photocurrent.

The typical current–voltage (*I*–*V*) characteristics of an n–n type organic solar cell with a Ag cathode measured in the dark and under 100 mW/cm² simulated sunlight (Newport product with an AM1.5G filter) are shown in Figure 1a. The device was fabricated by sequentially deposited F16ZnPc (20 nm), C₆₀ (55 nm), and then a 5 nm buffer layer of tris-8-hydroxy-quinolinato aluminum (Alq₃)^{7,8} between C₆₀ and the Ag cathode on a prepatterned ITO anode (sheet resistance of 13 Ω per square) in high vacuum (base pressure ~10^{–6} Pa) by thermal evaporation from Knudsen cells. An open circuit voltage of 510 mV relative to the Ag electrode and a short circuit of 0.25 mA/cm² were obtained for this device. The external quantum efficiency (EQE) measurements with and without light bias are shown in Figure 1b. The measured photocurrent comes from the joint contribution of two n-type materials. The collection of holes and electrons by ITO and Ag electrodes respectively reveals a new photovoltaic mechanism completely different from the exciton dissociation in D–A type organic solar cells.

Both F16ZnPc and C₆₀ are n-type organic materials,^{10–13} with the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of –6.9 and –5.2 eV for F16ZnPc and –6.2 and –4.5 eV for C₆₀, respectively. The energy alignment of the two n-type materials in our fabricated device is shown in Figure 2. Based on the known mechanism, the exciton dissociation can only happen through hole injection into C₆₀ and electron generation at the F16ZnPc side or electron injection into F16ZnPc and hole generation at the C₆₀ side,^{14,15} resulting in hole and electron collection at the Ag and ITO electrode respectively. Actually the observed photovoltaic effect is realized by the collection of holes at the ITO and electrons at the Ag electrode.

Thus a different mechanism is proposed to explain the observed photocurrent generation (Figure 2): Excitons are generated in both F16ZnPc and C₆₀ when white light is illuminated, followed by

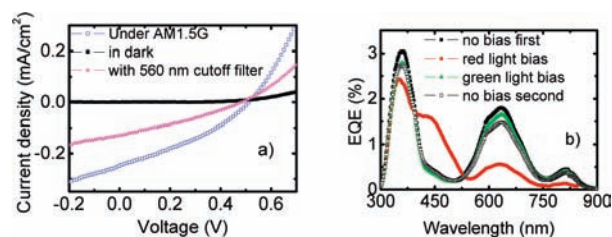


Figure 1. (a) *I*–*V* characteristics of the n–n type organic solar cell under AM1.5G simulated sunlight and in the dark. Short circuit current of 0.13 mA/cm² is still obtained even when a 560 nm cutoff filter is inserted between the AM1.5G source and the sample to filter out the light with wavelengths shorter than 560 nm. (b) EQE of the n–n type cell measured at 11 Hz with and without light bias. The measurements were conducted sequentially without bias, with red light bias, with green light bias, and without light bias again. In comparison to the first measurement without light bias, only an insignificant decrease of the measured signal without light bias again is observed after taking measurements under light bias, indicating there is only a small degradation during the measurements. The increase of EQE under red light bias in the range 400–530 nm is clearly in contrast with the almost unchanged value under green light bias. EQE is observable for the monochromatic light with wavelengths larger than 800 nm.

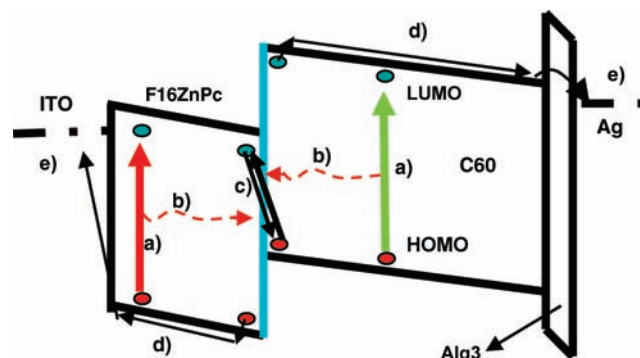


Figure 2. Device structure of an n–n type organic solar cell. The steps for producing photocurrent in the cell: (a) exciton generation by absorbing light in F16ZnPc and C₆₀, (b) exciton diffusion in F16ZnPc and C₆₀ to the interface, (c) intermolecular recombination at the interface (electron from F16ZnPc side recombines with hole from C₆₀ side) to produce free carriers, (d) the diffusion and drifting of freed carriers (holes at F16ZnPc side and electrons at C₆₀ side), (e) carrier collection at the electrodes.

diffusion to the F16ZnPc–C₆₀ interface. The recombination of electrons from the F16ZnPc side with the holes from the C₆₀ side frees the holes in F16ZnPc and electrons in C₆₀, respectively. The produced free holes and electrons would be driven to the ITO and Ag electrode respectively by the built-in electric field originated from the work function difference between the two electrodes. Thus half of the charge carriers in excitons are used for harvesting the photocurrent, and the remaining half of the carriers are lost by

recombination at the interface. The serial structure in a conventional organic solar cell^{5,16–18} also uses half of the carriers to generate photocurrent. Differently, the n–n type device in this work annihilates half of the carriers by direct intermolecular exciton recombination at the interface while, in the conventional serial structure, excitons are dissociated first in the subcells followed by recombination of half of the produced free carriers at the connection of two subcells. Thus to achieve high current output, the current balance of subcells in the conventional serial structure is the crucial factor, while exciton balance (a much easier controlled factor) becomes the critical one in the n–n type organic solar cell.

The importance of exciton balance and the proposed mechanism in Figure 2 are revealed by the EQE shown in Figure 1b. Differently from the conventional D–A type organic solar cell where EQE under light bias is smaller than that without light bias,^{3,9} the n–n type solar cell displays a jump of EQE over a range of 400–530 nm under red light bias. EQE measured without light bias is determined by excitons produced in both F16ZnPc and C₆₀ under certain monochromatic light and then their recombination. As shown in Figure 1b, over a range of 300–400 nm, where absorptions of both F16ZnPc and C₆₀ are large, a large number of balanced excitons can be produced on both sides of the interface for intermolecular recombination, resulting in a large photocurrent. In the range of 400–530 nm where the absorption of C₆₀ is much larger than that of F16ZnPc, the generated exciton balance on the two sides of the interface is bad, thus leading to low recombination and small EQE. However, when excitons are already produced on the F16ZnPc side by a red light bias, the excitons produced on the C₆₀ side by monochromatic light in the range 400–530 nm could have more opportunities to recombine with the existing excitons on the F16ZnPc side for the EQE jump. These results clearly indicate that a larger photocurrent is produced from a better exciton balance on the two sides of the interface for higher recombination, and no photocurrent enhancement could be produced if no such an exciton balance is created by a light bias. Indeed, as shown in Figure 1b, insignificant cell EQE change with a green light bias is seen because of only a few excitons generated on the F16ZnPc side by the green light bias due to its negligible absorption at this wavelength.

One could argue that some other processes might also contribute to the observed phenomenon, which includes (1) direct ionization by incident light,¹⁹ (2) exciton dissociation at organic–electrode followed by free carrier drifting and then recombination at an n–n interface,²⁰ (3) tunneling at the interface to dissociate the excitons. The large observed photocurrent with a 560 nm cutoff filter in Figure 1a can rule out the process (1) because more energetic light in the AM1.5G spectrum for possible production of direct ionization is filtered out. Significant EQE above a wavelength of 800 nm (1.55 eV) shown in Figure 1b is further evidence that the photocurrent is not from the direct ionization process. Process (2) is also very unlikely because the ITO–F16ZnPc interface is believed to be an Ohmic contact.¹² Process (3) might not be the main contribution to the large photocurrent because of the large energy barriers for both electrons and holes,²¹ and this conclusion is also confirmed by the EQE measurement in Figure 1b.

This new n–n type organic solar cell demonstrates valuable scientific significance and renders a new approach to using various economic materials for solar energy applications, especially an alternative way to choose stable materials in the fabrication of

organic solar cells. The performance could be also improved by further optimizations in future investigations, for example, using two materials with a large absorption overlap or producing more balanced excitons on both sides of the interface for larger photocurrent. Using a p-type material to substitute F16ZnPc, the enhanced hole transport ability could increase the power conversion efficiency significantly (the very poor hole mobility of F16ZnPc is one of the reasons for lower photocurrent in the new conceptual n–n type organic solar cells compared to donor–acceptor type organic solar cells). Alternatively, the photocurrent of the cell can be improved by enhancing the built-in electric field to increase the free carrier collection efficiency in terms of the cell working theory on interface recombination of excitons.

In summary, intermolecular exciton recombination rather than exciton dissociation is used to generate free carriers from bounded excitons with a demonstrated quantum efficiency over 3% by an n–n type organic solar cell. The substantial intermolecular exciton recombination shown in this work not only provides a new way to choose economic and stable organic materials in fabricating organic solar cells but also illustrates a new physical concept with scientific significance.

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Supporting Information Available: Further experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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