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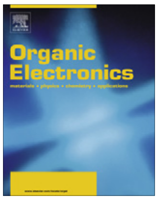

N,N′-diphenylperylene diimide functioning as a sensitizing light absorber based on excitation transfer for organic thin-film solar cells

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ABSTRACT

We demonstrated that N,N′-diphenylperylene tetracarbonic diimide (PTCDI-Ph) could work as an *n*-type sensitizing layer for the C_{60} *n*-type layer owing to interlayer excitation transfer (ET) when the PTCDI-Ph layer was placed between the C_{60} layer and the aluminum anode coupled with the bathocuproine layer. Well-aligned lowest unoccupied molecular orbitals between C_{60} and PTCDI-Ph (-4.55 eV for PTCDI-Ph and -4.5 eV for C_{60}) and a larger bandgap for PTCDI-Ph than C_{60} (2.04 eV for PTCDI-Ph and 2.0 eV for C_{60}) enabled this interlayer ET-based sensitization. Further, the optical interference effect could be also involved in the sensitization. It was also demonstrated that the combination of both *n*-type materials C_{60} and PTCDI-Ph could successfully reduce the amount of the expensive C_{60} used, and a thin C_{60} layer was indispensable for efficient charge separation. PTCDI-Ph could work as a light-harvesting *n*-type material incorporating C_{60}-based cells to compensate for C_{60}'s weak optical absorption.

1. Introduction

In recent years, organic photovoltaic (PV) cells have emerged as a promising solar cell technology, and the potential to fabricate flexible, lightweight devices with low material consumption and tunable absorption characteristics opens the way to a cost-efficient electricity supply [1,2]. Increasing research efforts have steadily improved power conversion efficiencies (PCEs) in small-molecule-based organic [3–6] and polymer-based [6–10] PV cells since the first efficient bilayer photovoltaic cell was reported by Tang [11]. Structurally well-defined small molecular materials avoid the inherent batch-to-batch physical property variations in polymers, and therefore, provide better reproducibility. In addition, they can be adapted for vacuum evaporation deposition techniques, which allow well-defined layer-by-layer structures to be built. Thus, vacuum evaporation–deposition fabricated organic small-molecule PV cells provide various potential future improvements to the PCE of organic PV cells—improvements which are still needed to make PV cells truly useful.

To enhance PCE, researchers must first increase the efficiency of light absorption and broaden the usable spectrum, which could be achieved by using more than two materials having complementary optical absorption properties. While organic PV cells fundamentally require two different materials, a *p*-type and an *n*-type material, for efficient charge separation, C_{60} fullerene derivatives, which

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are generally used as the *n*-type material, have weak optical absorption in the visible and near infrared (NIR) region because of their high symmetry. To compensate for this optical absorption problem with C_{60} derivatives, C_{70} and its derivatives, which exhibit stronger optical absorption owing to their lower symmetry [12], have been frequently used as the *n*-type material [13–15]. However, C_{70} and its derivatives are more expensive than C_{60} and its derivatives, which are already costly enough, because pristine C_{70} is only obtained as a by-product of C_{60} production. Using C_{70} and its derivatives, instead of C_{60}, to pursue higher PCE would, therefore, not be commercially viable. Another way to improve absorption efficiencies of the *n*-type layer in the visible-to-NIR region is, therefore, required. From the viewpoint of efficient charge separation and collection, fullerene derivatives are indispensable for forming the *p*/*n* heterojunction, so, it might seem that there is no practical solution to the problem described.

However, we have recently demonstrated the use of two *p*-type layers with complementary optical absorption properties [16]. Interlayer excitation transfer (ET) between the two layers leads to a relay of excitonic energies to the *p*/*n* junction, resulting in the sensitization of the organic PV. If the same system could be adopted for *n*-type materials, it would successfully allow the indispensable fullerene-based *n*-type layer system to be given higher optical densities. Thus, costly fullerene-based materials would not be required to achieve higher optical absorptions. In addition, it would probably be possible to reduce the amount of C_{60} used because the thin C_{60} layer in the *n*-type material is only used for charge separation. Therefore, it is necessary to explore the possibility of creating a light-harvesting *n*-type material incorporating fullerene-based organic PV cells to compensate for the fullerenes' weak optical absorption.

Here, we demonstrate that N,N′-diphenylperylene tetracarboxylic diimide (PTCDI-Ph, see Fig. 1a) can work as an *n*-type sensitizing layer for the indispensable C_{60} *n*-type layer when the PTCDI-Ph layer is placed between the C_{60} layer and the metal anode, which requires a thin bathocuproine (BCP) buffer layer, as shown in Fig. 1b.

2. Experimental

Fig. 1b shows a schematic of the device structure used in the study, and Fig. 1a shows the chemical structures of the materials used. In this study we employed a (thiophene/phenylene) co-oligomer, α,ω-bisbiphenyl-*ter*-thiophene (BP3T), as the *p*-type material instead of more commonly used materials such as copper phthalocyanine (CuPc). This is because we aimed to determine exactly how the PTCDI-Ph layer works in organic photovoltaic devices. PTCDI-Ph (Dainichiseika Color & Chemicals), BP3T (Sumitomo Seika Industries), C_{60} (Frontier Carbon), and BCP (TCI) were purified using temperature-gradient train sublimation with an Ar gas flow before use. We prepared the devices by depositing several materials sequentially onto commercially available indium–tin–oxide (ITO) coated glass substrates, which had a sheet resistance of 15 Ω/square. The substrates were first washed with aqueous detergent, pure water, and 2-propanol with ultrasonification and then treated with O_2 plasma at 50 W for 5 min. We prepared a poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) layer on the substrates by spin-coating with a commercially available formula (Clevios P AI 4083, H.C. Starck), before depositing several organic layers by thermal evaporation under vacuum ($<2.0 \times 10^{-4}$ Pa) at the rate of 0.5 Å/s. Finally, the aluminum electrode was prepared on top of the organic layer stack by thermal evaporation in a vacuum, at the rate of 10 Å/s. Active areas of the cells were approximately 6 mm^2. We transferred the devices produced into a highly inert glove box (O_2 concentration 5 ppm, dew point <−50 °C) with no exposure to ambient conditions, and then mounted them in a small chamber, which had a quartz window, in the glove box. A source meter (Keithley, 2410) was

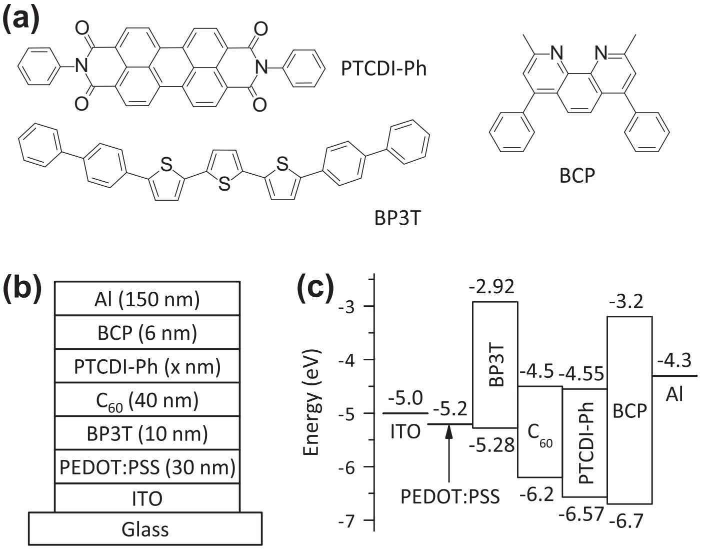

Fig. 1. (a) The structures of the chemicals used and their abbreviations, (b) the sectional cell structure, and (c) energy diagram of the PV cell proposed in this study.