

Temperature-dependent device performance of organic photovoltaic cells based on a squaraine dye



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ABSTRACT

We have systematically investigated the temperature-dependent device performance of organic photovoltaic (OPV) cells based on a squaraine dye. The 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl] squaraine:[6,6]-phenyl C₇₁ butyric acid methyl ester (DIBSQ:PC₇₀BM) OPV devices were fabricated and characterized under 100 mW cm⁻² (AM1.5G solar spectrum) in a temperature range from 285 to 360 K. The temperature-dependent photovoltaic parameters such as open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) were studied in detail. The increasing temperature led to an improvement of J_{sc} and FF, which should be ascribed to the enhanced carrier mobilities and improved electrode/active layer contact thus the improvement of photocurrent extraction at an elevated temperature. However, the V_{oc} decrease in the same period due to the carrier recombination of the OPV device. The increase in the J_{sc} and FF overtakes the decrease in the V_{oc} with increasing temperature, resulting in a significantly improved PCE at elevated temperature. This study indicated that the DIBSQ based BHJ cells has promising potential for the practical application under changeable temperature environment.

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1. Introduction

Organic photovoltaic (OPV) cells have shown great potential as renewable energy sources because of their promising features, which include compatibility with large-area and low-cost coating techniques, lightweight and device flexibility [1–5]. Solution-processed small molecular bulk-heterojunction (BHJ) OPV cells have been demonstrated to be a competitive alternative to their polymeric counterparts because of their attractive advantages, which include facile material synthesis and purification, and tunable molecular structures and energy levels [6–13]. Among various small molecule OPV materials, squaraine (SQ) dyes have shown promising potential as electron donors due to their high absorption coefficients of 10⁵ cm⁻¹ and intense absorption in visible and near-infrared (NIR) spectral regions [14–17]. These fascinating features make SQ materials being considered as attractive donors for high-efficiency OPV cells. Researchers have

focused on improving device performance of SQ-based OPV cells by using various strategies, such as developing efficient SQ donors [18,19], optimizing device structure [20,21], controlling film morphology of SQ:fullerene photoactive layers [22,23] and incorporating effective interlayers [24].

The 2,4-bis[4-(*N,N*-diisobutylamino)-2,6-dihydroxyphenyl] squaraine (DIBSQ) is one of the most efficient electron donor materials in SQ dye-based OPV cells. DIBSQ has an absorption coefficient of as high as over 3 × 10⁵ cm⁻¹, indicating that about 10 nm-thick DIBSQ films may cause significant absorption and photocurrent generation [21]. Moreover, the highest-occupied molecular orbital (HOMO) and lowest-unoccupied molecular orbital (LUMO) levels of DIBSQ are located at -5.3 and -3.5 eV, respectively, which provide a high open-circuit voltage (V_{oc}) of near 1.0 V in the OPV device [23]. Great efforts have been made for achieving high-efficiency DIBSQ based OPV cells. Forrest and Thompson firstly used a vacuum evaporation technique to obtain an efficient planar heterojunction (PHJ) DIBSQ/C₆₀ device, which demonstrated a remarkable power conversion efficiency (PCE) of 3.1% [25]. The DIBSQ/C₆₀ PHJ devices were later fabricated by using solution-processed thin films of DIBSQ combined with vacuum-evaporated C₆₀, obtaining a much higher PCE of 4.6% through

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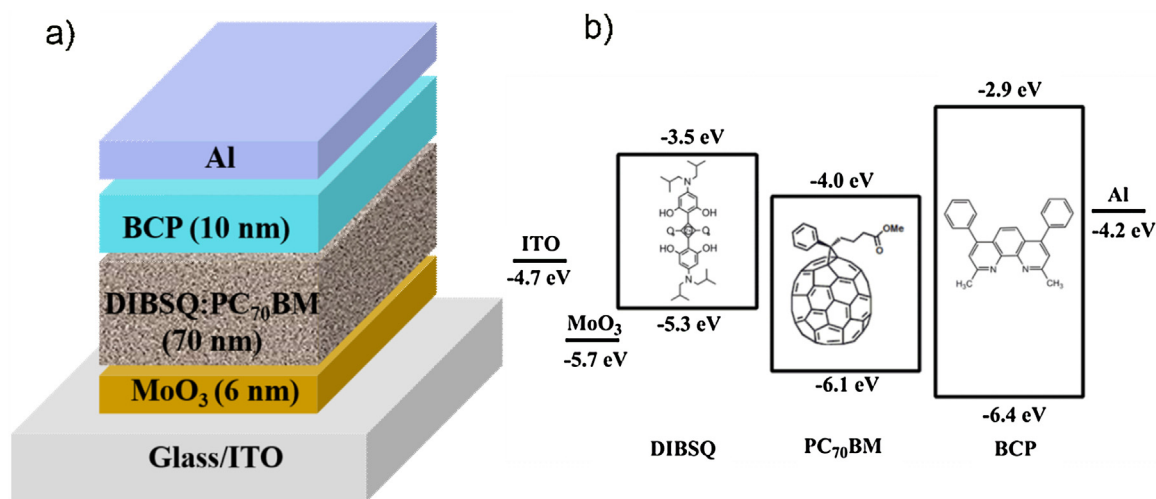


Fig. 1. (a) Device architecture and (b) schematic energy level diagram of the DIBSQ:PC₇₀BM BHJ cell.

morphology control of the DIBSQ film [26]. Wei et al. applied the blend film of DIBSQ and [6,6]-phenyl C₇₁ butyric acid methyl ester (PC₇₀BM) as photoactive layer to construct a solution-process OPV device, which realized a PCE of 2.7% [27]. Later they focused on the DIBSQ:PC₇₀BM OPV system and employed the solvent annealing treatment to optimize the film morphology of the active layer, realizing a PCE of 5.2% [28]. Chen further improved the PCE of the DIBSQ:C₇₀ active layer-based BHJ cell up to 6.1% by using the vacuum co-evaporation technique [29]. In addition to the high device performance, the DIBSQ-based BHJ cells also possessed other beneficial properties for practical application. Our recent results demonstrated that the device performance of DIBSQ:PC₇₀BM BHJ cells was sensitive to the operating temperature [23]. When the photovoltaic cells are exposed to intense sun irradiance, there is usually an increase in the operating temperature of the device, particularly some places near Earth's Equator. The study on the influence of operating temperature on device performance of the DIBSQ-based BHJ cells is critical to further explore their potential practical application under changeable temperature environment.

In this work, we prepared the DIBSQ:PC₇₀BM BHJ cells and then measured the device performance at various operating temperature. Thereafter we present a detailed analysis of the temperature-dependent main parameters of the OPV device, i.e. short-circuit current density (J_{sc}), V_{oc} , fill factor (FF) and PCE, to systematically study the temperature-dependent device performance of the DIBSQ:PC₇₀BM BHJ cells.

2. Experimental

All chemicals and solvents were used as received. DIBSQ dye was synthesized according to the procedure reported in the literature [30]. Target compound was confirmed to be analytically pure by ¹H-nuclear magnetic resonance (NMR) and elemental analysis and >99.9% pure by high-performance liquid chromatography (HPLC).

The DIBSQ:PC₇₀BM BHJ cells were fabricated as follows: patterned indium-tin-oxide (ITO) coated glass substrates were cleaned using detergent, deionized water, acetone and isopropanol in an ultrasonic bath. Cleaned substrates were dried and kept in an oven at 80 °C. Substrates were exposed to UV ozone for 30 min, and then were immediately transferred into a high-vacuum chamber (1×10^{-5} Pa) for the deposition of 6 nm-thick MoO₃. Photoactive layers (thickness: 70 ± 5 nm) were fabricated by spin-coating DIBSQ:PC₇₀BM solution (20 mg mL⁻¹ in chloroform with a blend

ratio of 1:5) on the MoO₃ coated ITO surface in the N₂-filling glove box, followed by thermal treatment at 70 °C for 10 min. Finally, the substrates were transferred back to a high-vacuum chamber where bathocuproine (BCP) (10 nm) and Al (100 nm) were deposited as the top electrode. The active area of cells is 0.04 cm² defined by the overlap of the ITO anode and the Al cathode. The final device structure was ITO/MoO₃ (6 nm)/DIBSQ:PC₇₀BM (70 nm, 1:5)/BCP (10 nm)/Al (as shown in Fig. 1a). The energy level diagram and the molecular structures of organic molecules used in this work were shown in Fig. 1b. The structures of hole-only and electron-only devices were ITO/MoO₃ (6 nm)/DIBSQ:PC₇₀BM (70 nm, 1:5)/MoO₃ (6 nm)/Al and ITO/Cs₂CO₃ (2 nm)/DIBSQ:PC₇₀BM (70 nm, 1:5)/BCP (10 nm)/Al, respectively. All the devices were put on a temperature-controlled bench for carrying out current density–voltage (J – V) and external quantum efficiency (EQE) characterizations. Because the poor stability of cathode buffer BCP causes the amorphous film to crystallize easily under high temperature (which will clearly decrease the device efficiency) [23], we tested the device performance in a temperature range from 285 to 360 K. Bright state J – V characteristics were measured using a programmable source meter (Keithley 2400) under simulated 100 m Wcm⁻² irradiation with an AM 1.5G simulated solar spectrum. The EQE spectra of the devices were measured under standard measurement conditions on a 7-SCSpec solar cell measurements system manufactured by 7-STAR Co. The UV–vis absorption spectra were recorded at room temperature using an ultraviolet spectrophotometer (HITACHI U-3900H).

3. Results and discussion

3.1. OPV performance

Fig. 1 represents the architectures of the DIBSQ:PC₇₀BM BHJ device (Fig. 1a) and the corresponding energy-level diagram (Fig. 1b) in this study. In this BHJ device, the MoO₃ is adopted as anode buffer layer while the BCP acted as cathode buffer layer, the DIBSQ:PC₇₀BM blend film is the photoactive layer. The thickness and blend ratio of the DIBSQ:PC₇₀BM film are 70 nm and 1:5, respectively, which are the optimized parameters for high performance DIBSQ:PC₇₀BM BHJ devices demonstrated by our previous results [23].

Fig. 2 shows the absorption spectra of thin films of neat DIBSQ, PC₇₀BM and the blend DIBSQ:PC₇₀BM (70 nm, 1:5). The spectrum of the DIBSQ film exhibits an absorption band from 500 up to 800 nm with λ_{max} = 680 nm; the spectrum of PC₇₀BM film shows

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