



Boron subphthalocyanines as electron donors in outdoor lifetime monitored organic photovoltaic cells

Richard K. Garner^a, David S. Josey^a, Stephanie R. Nyikos^a, Aleksa Dovijarski^a, Jon M. Wang^a, Greg J. Evans^a, Timothy P. Bender^{a,b,c,*}

^a Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5

^b Department of Materials Science Engineering, University of Toronto, 180 College Street, Toronto, Ontario, Canada M5S 3E4

^c Department of Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5

ARTICLE INFO

Keywords:

Subphthalocyanine

Lifetime

Donor

Structure

Outdoor

Photovoltaic

ABSTRACT

Structural variants of boron subphthalocyanines were tested as light absorbing and electron donating materials paired with C₆₀ in organic photovoltaic cells, in a rooftop ambient environment according to ISOS-O3 protocols. Constant current monitoring and daily current-voltage sweeps, reinforced by irradiance and temperature tracking, reveal differing degradation rates depending on the chemical structure of the boron subphthalocyanine. Results suggest that the observed initial burn-in efficiency loss observed in all devices is due to C₆₀, but that the longer term degradation trend is attributable to the chemical breakdown of the subphthalocyanine donors through hydrolysis. These findings demonstrate that the molecular structure of boron subphthalocyanines is a significant handle on device longevity, and that a structure-property relationship can be established for stability. The results also highlight the need for alternative electron accepting materials to C₆₀ for pairing with boron subphthalocyanines in planar heterojunction solar cells, as well as the necessity of a more robust encapsulation methodology.

1. Introduction

Organic photovoltaic devices, or OPVs, are currently being explored as low-cost sustainable energy sources. OPVs are considered to be promising due to their predicted ease of manufacturing and relatively inexpensive photo- and electro-active materials, in comparison to commercial inorganic photovoltaics [1,2]. The family of functional organic electronic materials known as boron subphthalocyanines (BsubPcs), headed by the prototypical chloro boron subphthalocyanine (Cl-BsubPc), are undergoing active research due to their relatively high power conversion efficiencies (PCEs), ease of synthesis and processing, and physical tenability [3–5]. A record in the field of planar heterojunction (PHJ) OPVs, the 8.4% power conversion efficiency achieved by Cnops et al., [6] was recently set by using a device containing Cl-BsubPc and chloro boron subnaphthalocyanine (Cl-BsubNc) as an electron acceptor and bifunctional layer respectively. For use as an electron donor material in PHJ OPVs, BsubPcs are most frequently paired with a C₆₀ electron acceptor [5,7,8].

BsubPcs have the useful chemical property that their axial and peripheral positions can be functionalized with a variety of substituents and molecular fragments [9]. Instead of the prototypical axial chlorine

atom, other halogens or organic fragments can be easily substituted in place. This allows for the adjustment of the molecule's properties, including the solid state arrangement and distribution of its energy levels [10]. The benefits of the latter are twofold: First, energy levels can be tuned to provide efficient exciton dissociation with acceptors in bilayer PHJ structures or with other layers in cascade architectures. Second, the absorption spectra can be shifted to different wavelengths, [9] such that a device incorporating multiple BsubPcs could absorb a wider fraction of the solar spectrum [11]. This incorporation can be accomplished via the use of cascade architectures or co-deposited layers, some of which have shown signs of organic alloying effects [11]. The versatility of BsubPcs in both chemical synthesis and device engineering make them a continually attractive candidate for future OPV research.

While BsubPcs and other materials are being harnessed to provide ever increasing PCEs, there is as yet insufficient clarity regarding their long term stability. Even where lifetime studies have taken place, the variety of degradation mechanisms and test conditions used have rendered direct comparisons difficult [12]. Efforts such as ISOS, the International Summit on OPV Stability, have recognized that further emphasis is required in order to identify which molecular lineages are likely to yield an industrially useful result. ISOS has produced

* Corresponding author at: Department of Chemical Engineering and Applied Chemistry, University of Toronto, 200 College Street, Toronto, Ontario, Canada M5S 3E5.
E-mail address: tim.bender@utoronto.ca (T.P. Bender).

consensus standards for OPV stability testing which establish various testing protocols. These protocols allow results to be compared more easily between laboratories, and we have therefore used them in this study [13].

Various photo-stability parameters of BsubPcs have been explored in films. González-Rodríguez et al. measured the thermal stability of several BsubPc compounds, [14] and Yamasaki and Mori measured the thermal and photostability of many BsubPc molecules including the three explored here [15]. Both found more rigid BsubPc axial bonds to be more stable, with Yamasaki and Mori finding a stability trend of Ph-BsubPc > Cl-BsubPc > PhO-BsubPc. Our own group found that the photostability of BsubPcs was not significantly impacted by substituting a phenoxy axial ligand for the typical halide, in an analysis of BsubPcs incorporating peripheral solubilizing groups and doped into thin polystyrene films [16]. As we show below, these film-based trends were not predictive of molecular longevity in encapsulated OPV devices.

More or equally relevant to this study, previously explored degradation mechanisms for BsubPcs/C₆₀ OSCs are discussed in detail by Wang et al. [17] and Tong et al. [8] They both indicate the formation of trap states in C₆₀ as the dominant contributor to burn-in degradation, with similar effects observed in analogous phthalocyanines/C₆₀ devices [18]. Burn-in refers to the sharp loss in efficiency measured after the first day of irradiation. To explore these mechanisms, we tested an α -sexithiophene/C₆₀ (α -6T) PHJ OPV device set, which was used as a point of comparison to help understand the initial burn-in degradation behaviour of the OSCs.

This paper presents our investigation of the stability of several BsubPc compounds under outdoor solar irradiation in a PHJ OPV electron donor arrangement with a C₆₀ acceptor (Fig. 1). Our testing was performed at the ISOS-O3 level, the most rigorous grade of outdoor lifetime monitoring, with further details and minor exceptions reported in the Supporting information (SI). The primary goal was to identify whether a structure-property relationship exists between the choice of axial substituents of various BsubPc molecules and the stability of those molecules in devices. The first compound is the prototypical Cl-BsubPc, followed by our previously reported phenoxy-BsubPc [9] (PhO-BsubPc) and phenyl-BsubPc [19] (Ph-BsubPc). Each of these compounds differ only by the axial substituent, which is sufficient to cause devices to vary slightly in their post-fabrication metrics.

In conjunction with this study, our lab has also undertaken a similar stability investigation of the same set of three BsubPcs as electron acceptors [20]. This effort found no evidence of a burn-in effect, which is attributable to the lack of fullerene/C₆₀ in the devices. The degradation trends identified for each material matched those determined by this study, indicating a true structure-property relationship between molecular design and stability under solar irradiance.

2. Materials and methods

All BsubPc compounds (Cl-, Ph- [19] and PhO-BsubPc [9]) were synthesized and purified internally according to our established

procedures. The C₆₀ was purchased from SES Research, and α -6T was bought from Lumtec. These compounds were all purified via train sublimation. Bathocuproine (BCP) was purchased from Sigma Aldrich, molybdenum (VI) oxide (MoO_x) from Strem Chemicals, and silver from R. D. Mathis Company, all of which were used as-received. PEDOT:PSS from Heraeus was filtered with 0.22 μ m syringe filters. Devices with an area of 0.2 cm² were constructed on ITO-coated glass, using a spin-coated PEDOT:PSS layer, a MoO_x hole transport layer, and a BCP electron transport layer. BsubPc donor layers were 10 nm thick, α -6T layers were 50 nm thick, and fullerene layers were 30 nm thick, all in accordance with past optimized devices [3,11]. Deposition of organic molecules and metals was performed via evaporation from boron nitride crucibles with a chamber pressure of approximately 1×10^{-7} Torr, using a calibrated QCM used to monitor thickness. Devices were encapsulated against atmosphere using a surficial 100 nm MoO_x buffer layer followed by Ossila encapsulation epoxy and a thin sheet of glass. This resulted in the device structure shown in Fig. 1. Devices underwent initial current-voltage (JV) testing before removal from the glovebox. This process used a Keithley 2401 SourceMeter, with light provided via an Oriel 300 W xenon arc lamp using an AM1.5G filter. Intensity was set to 100 mW/cm² using a calibrated silicon photodiode.

OPV cells were then placed outside for roughly six hours daily, taken indoors at night or to avoid precipitation. Constant current monitoring used USB data acquisition devices, with OPV cells facing due south. A tilt angle of roughly 43.7° was used, corresponding to the latitude of the University of Toronto. Temperature was recorded using a thermocouple on the back of a device substrate. Solar irradiance data was gathered via a pyranometer placed parallel to the ground several meters away. Irradiance values were transformed to those for a 43.7° tilted array using the model developed by Erbs et al., [21] as implemented programmatically by Josey et al. [20] Daily JV curves were recorded each morning using the same method as the initial post-fabrication test. Humidity, air temperature, wind speed, and wind direction, were recorded simultaneously in accordance with ISOS-O3 standards, [13] and are plotted in Figures S1 and S2 of the SI. An image of the rooftop testing apparatus can be found in Figure S4 of the SI.

3. Results and discussion

The BsubPc molecular variants used in this study were chosen to investigate the susceptibility of various axial substituents to degradation with an OPV device. The Cl-BsubPc, in addition to being the prototypical BsubPc compound, was selected to test the vulnerability of a halide substituent. The Ph-BsubPc, previously examined for its alternative BsubPc crystal packings, [19] was another interesting candidate due to the rigid boron-carbon bond yielding a perpendicular phenyl molecular fragment. The PhO-BsubPc, which has demonstrated much greater solubilities than other BsubPcs, was selected for its bent oxygen linkage [9]. The initial post-fabrication metrics of the devices made using these molecules are tabulated in Table 1. The device structure is our lab's standard for testing BsubPc derivatives as electron donating

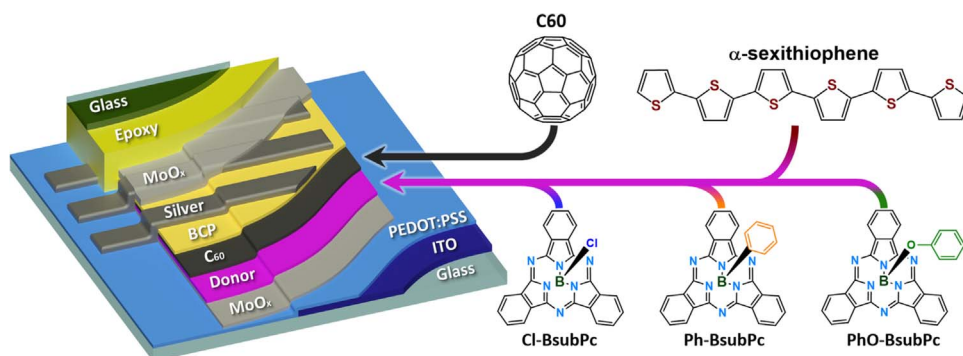


Fig. 1. The full device layer stack is shown at left. Molecular structures of compounds (used independently) in active layers are shown at right.

Download English Version:

<https://daneshyari.com/en/article/6534470>

Download Persian Version:

<https://daneshyari.com/article/6534470>

[Daneshyari.com](https://daneshyari.com)