



Assessing the stability of high performance solution processed small molecule solar cells



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ABSTRACT

Solution-processed small molecule-fullerene bulk heterojunction (SM BHJ) solar cells now have power conversion efficiency (PCE) greater than 10%. However, degradation of SM BHJ solar cells has not been well studied. This work reports the first stability study of six high performance molecules including the record SM BHJ solar cells under device operating conditions. Solar cells with a range of donor molecular weight from 1200 to 2300 Da giving 6–10% PCE are monitored in nitrogen gas under 1 sun illumination with maximum power point tracking as well as at 25 °C and 70 °C in the dark. Both heat and light contribute to initial exponential decay or burn-in with total reduction in efficiency from 31% to 66%. Larger molecules are found to be resistant to heat induced burn-in, while more crystalline active layers are more resistant to light induced burn-in. After burn-in, the linear degradation is observed to be governed by thermal processes. Stabilized TS80 lifetimes of the SM BHJ solar cells range from 3450 h to 5600 h. Molecular design towards higher stability should aim at increasing thermal stability while maintaining crystallinity for photostability.

1. Introduction

While organic photovoltaics (OPV) have traditionally utilized semiconducting polymer materials, over the past several years there has been a growing interest in monodisperse small molecules. Compared to polymers, solution processed small molecules are easier to purify and could be more stable with a well-defined molecular weight (MW) [1,2]. When molecules are blended with fullerenes in the bulk heterojunction (BHJ) active layers of a solar cell, the power conversion efficiency (PCE) can now reach over 10% [3–9]. With these promising traits of the molecules, the operating stability remains a critical missing piece of information for projecting practical implementation against competing technologies [10,11].

The degradation mechanisms of polymer solar cells (PSCs) are reasonably well understood and provide background for degradation of solution-processed small molecule bulk heterojunction (SM BHJ) solar cells because both active layers use fullerene and have a BHJ structure.

Two regimes of degradation are usually found in OPV: an initial exponential burn-in followed by a slower linear degradation [10]. There are two definitions of lifetime: T80 lifetime and TS80 stabilized lifetime. T80 lifetime is defined by the time it takes a solar cell to degrade to 80% of its initial PCE, which could be within the exponential burn-in period since OPV could burn-in more than 20% [12,13]. On the other hand, TS80 stabilized lifetime is defined by the time it takes a solar cell to degrade 80% after it is burned-in [14]. There are five primary stresses that have been identified to shorten the lifetime of organic solar cells: oxygen, moisture, heat, UV light and visible-near infrared light [11,15–19]. In air, a crystalline and dense neat polymer film photo-oxidizes and bleaches more slowly than an amorphous film of the same material because the molecules are confined and are less able to undergo chemical reactions [15,20]. With a UV filter and encapsulation to remove oxygen and moisture, a polymer solar cell can have a TS80 lifetime of 20 years [13]. In encapsulated PSCs, thermal degradation occurs around a glass transition temperature, above which

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the polymer and fullerene can move and form a blocking layer at an interface, causing the FF to drop [21,22]. Photo degradation in encapsulated PSCs can occur within the active layer due to photochemical processes, causing an open circuit voltage (V_{oc}) loss, [19,23] but are suppressed in PSCs with ordered active layers [24,25]. Fullerene dimerization has also been observed when PSCs with PC₆₀BM are aged under light, [26–29] which results in J_{sc} loss; this effect is particularly enhanced in strongly phase separated systems with pure polymer and fullerene domains [27,28].

While extensive lifetime testing has been performed on PSCs, lifetime tests have been limited to dark storage stability in SM BHJ solar cells [4,30,31]. The lifetime under real operating conditions has not yet been measured. The goals of this study are to report for the first time both the extent of degradation of top performance SM BHJ solar cells aged under real operating conditions and provide guidelines for designing next generation small molecules for thermally and photo stable solar cells.

We have investigated the degradation of six of the highest performing SM BHJ solar cells that were available when this project began. They have PCE ranging from 6% to 10%. [3,6,7,32,33]. The molecules can be divided into two groups of similar chemical structures, as shown in Fig. 1. T1, X2 and F3 have alternating Si-cyclopentadithiophene and benzothiadiazole cores with alkyl-bithiophene endcaps, while DRCN5T, DRCN7T, and DR3TSBDT or the “DR family” have oligothiophene and dialkylthiol-substituted benzodithiophene cores and rhodanine endcaps. Table 1 shows each solar cell stack and its initial performance. We avoid UV, oxygen, and moisture since they are well known to make the organic materials degrade and can be avoided with suitable packaging.[13] We study the effect of visible-near infrared light and heat at 70 °C, the operating temperature, [34,35] on degradation of SM BHJ solar cells beyond 3000 h. We investigate and decouple the effects of dark storage in N₂, thermal and photo degradation, which all can play a role in performance decline. We use grazing incident X-ray diffraction (GIXRD) to characterize the morphology of optimized SM BHJ blend films and neat small molecule thin films that have been aged thermally.

2. Materials and methods

2.1. Solar cell preparation

All solar cells were made on ITO-patterned glass substrates (15 Ω/square, Xinyan Technologies LTD).

2.1.1. Substrate cleaning

Substrates for solar cells were first scrubbed with 1:10 dilute Extran 300 detergent: De-ionized (DI) water, then ultrasonicated in the same

solution for 15 min. After, they were rinsed in DI water five times and ultrasonicated in acetone and isopropyl alcohol baths for 15 min each. Finally, the substrates were blown dry with nitrogen gas and placed in a covered petri dish in an oven (95 °C) overnight to remove any residual solvent.

2.1.2. T1 solar cells fabrication

ITO-coated glass substrates were removed from the oven and treated with UV-Ozone plasma for 15 min. Then a PEDOT: PSS solution (Clevios PVP AI 4083) was spun onto the substrates in ambient atmosphere and baked at 140 °C for 10 min, which resulted in a film thickness of about 30 nm. The substrates were quickly transferred into a glovebox with < 10 ppm oxygen and < 10 ppm moisture for active layer deposition. The T1:PC₇₀BM solution with 3:2 weight ratio and 0.4% diiodooctane by volume with an overall concentration of 35 mg/mL in chlorobenzene was prepared the night before and kept on a stirring hotplate at 90 °C. The solution was filtered and spun at 1750 rpm for a minute at maximum acceleration, which gave a 100-nm-thick active layer. The films were dried on a hotplate at 70 °C for 10 min and then were transferred to a dry glovebox for top electrode deposition. 7 nm Ca and 150 nm Al were thermally evaporated one after the other on top of the active layer at a background pressure less than 10⁻⁶ Torr. The active area of each solar cell device is 0.1 cm².

2.1.3. X2 and F3 solar cells fabrication

ITO-coated glass substrates were removed from the oven and transferred directly into a dry glovebox with < 10 ppm oxygen and < 10 ppm moisture. 10 nm MoO_x was thermally evaporated onto the ITO at a background pressure less than 10⁻⁶ Torr. The substrates were then transferred into a solvent glovebox, with the same level of oxygen and moisture as the previous glovebox, for active layer deposition without any exposure to ambient atmosphere. The active layer solutions of X2:PC₆₀BM and F3:PC₆₀BM with 1:1 weight ratio with an overall concentration of 20 mg/mL in chloroform solution were prepared and kept on a stirring hotplate at 55 °C the night before. The hotplate temperature was brought down to 25 °C just before active layer spinning with the hotplate still stirring. The active layer solution was spun at 2000 rpm for 40 s at 1500 rpm per second acceleration, which both yielded 100 nm thickness. The substrates were then transferred back to the dry glovebox for top electrode deposition. 7 nm Ca and 150 nm Al were thermally evaporated one after the other on top of the active layer at a background pressure less than 1×10⁻⁶ Torr. The active area of each solar cell device is 0.1 cm².

2.1.4. DRCN5T, DRCN7T, and DR3TSBDT solar cells fabrication

DRCN5T, DRCN7T, and DR3TSBDT solar cells were made at Nankai University and completed at Stanford University. ITO-coated

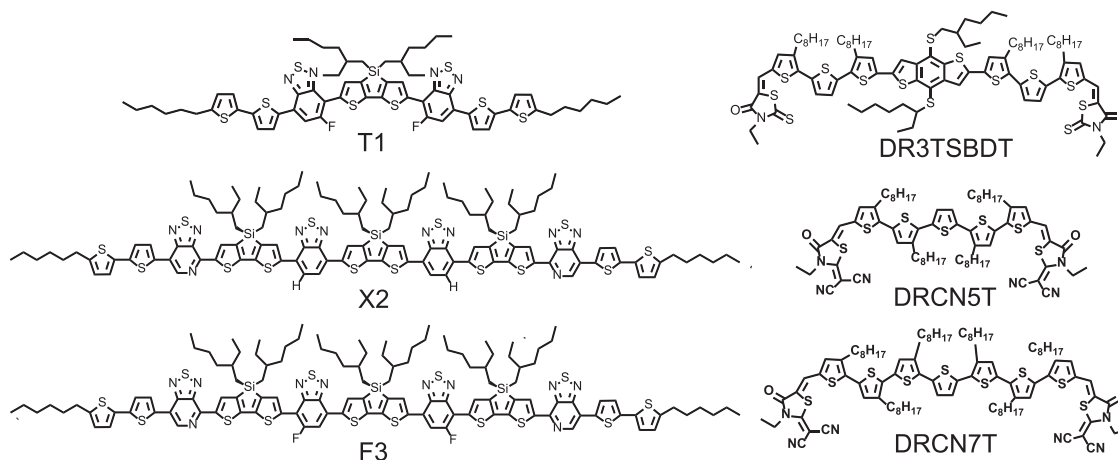


Fig. 1. Chemical structure of solution processed small molecules.

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