

Solar Cells from a Solution Processable Pentacene with Improved Air Stability

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This manuscript describes photovoltaics from 6,13-di(2-thienyl)pentacene¹ that exhibit improved stability in ambient atmosphere. Photovoltaics are currently undergoing intense scrutiny for the inexpensive and renewable production of electrical energy.^{2–5} Within the broad and diverse photovoltaic field, organic small molecules are promising materials for further research and development because they can be easily synthesized and purified.⁴ Moreover, they are monodisperse, exhibit relatively high carrier mobilities, and can be processed directly from solution.⁴

Several groups have recently reported organic photovoltaics utilizing pentacene and buckminsterfullerene (C₆₀) with peak efficiencies up to 1.6%.^{6–15} Pentacene is a natural choice as an electron donor material in such devices because it has been extensively studied in field effect transistors¹⁶ and can be modified for improved solution processability.^{10,11,15} However, upon exposure to oxygen, pentacene-based devices decay rapidly,^{13,14} presumably because of photo-oxidation of

the pentacene donor.¹⁶ This situation is exacerbated by the fact that nearly all organic solar cells necessitate complex structures, low work function cathodes, and/or extensive encapsulation to achieve peak performance.^{1–5} Surprisingly, the molecular design of pentacenes for improved stability in the presence of oxygen, an absolutely crucial issue, has received little attention to date.^{13,14}

Previously, we have reported the synthesis of 6,13-di(2-thienyl)pentacene, an air-stable and solution-processable pentacene derivative.¹ Films from this molecule are amorphous with no long-range order. Nonetheless, this material has relatively high p-type carrier mobilities and exhibits excellent performance in ambient-operated transistors, presumably because of strong π – π stacking interactions in the solid state. These properties of 6,13-di(2-thienyl)pentacene have encouraged us to investigate its performance in solar cells.

The bilayer photovoltaic device structure is shown in Figure 1.¹⁷ We spincoat PEDOT:PSS (H. C. Starck) onto patterned ITO (LUMTEC) to thickness of approximately 25–30 nm. As the p-type donor material, we subsequently spincoat 6,13-di(2-thienyl)pentacene to a ~15 nm thickness onto the PEDOT:PSS layer. As the n-type acceptor material, we deposited 40 nm of buckminsterfullerene (NanoC) on top of the thienyl pentacene layer. To complete devices with an active area of 0.16 cm², we deposited 60 nm of aluminum as the cathode. Subsequently, the devices were characterized in ambient atmosphere/room temperature without thermal annealing, which was not found to significantly affect device performance. Electrical testing was performed with and without AM 1.5 simulated solar illumination, and the illumination intensity was calibrated versus a silicon photodiode.

To gain insight into the pentacene morphology, we examined the 6,13-di(2-thienyl)pentacene films with atomic force microscopy (see the Supporting Information). The spin-coated films are essentially featureless with a root mean square roughness of ~1–2 nm. The morphology is far smoother than that typically found for deposited pentacene, which has roughnesses on the order of tens of nanometers.¹² Such smooth films are expected to enhance device stability by preventing microscopic short circuits in thinner regions.^{10,18}

Typical J – V characteristics for a 6,13-di(2-thienyl)pentacene photovoltaic device with and without illumination are shown in Figure 2. In ambient atmosphere, the device exhibits diode behavior. The short circuit current density of $J_{sc} = 4.2$ mA/cm², open circuit voltage of $V_{oc} =$

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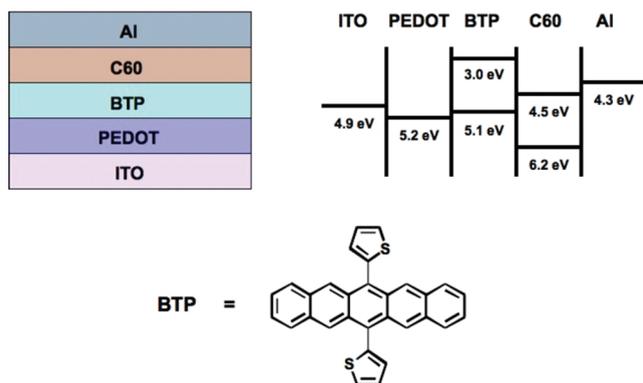


Figure 1. Schematic illustration of the device architecture and the corresponding energy levels (reported with respect to vacuum) for each material. Note the structure of 6,13-di(2-thienyl)pentacene.

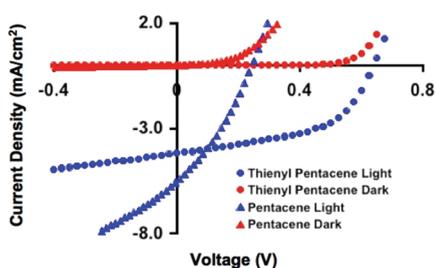


Figure 2. J - V curves for both a 6,13-di(2-thienyl)pentacene device and an unsubstituted pentacene reference device with (blue) and without (red) illumination at 100 mW/cm^2 . The unsubstituted pentacene device has 25 nm of thermally evaporated pentacene layer as the donor layer.

0.63 V, and fill factor of $FF = 0.53$ result in a peak power conversion efficiency of 1.4% .¹⁹

It is important to note here that despite the lack of a low work function cathode and/or a hole blocking layer, the overall efficiency of 6,13-di(2-thienyl)pentacene devices compares favorably to that of more complicated devices from unsubstituted pentacene.^{6–9,12–14} In fact, a reference device that utilized unsubstituted pentacene as the donor and was prepared/tested under very similar conditions, yielded an efficiency of 0.4% , which is comparable to literature values for an identical device structure (Figure 2).⁹

The performance of 6,13-di(2-thienyl)pentacene in a simple device architecture can also be partially ascribed to the high open circuit voltage. Although many experimental factors can influence the V_{oc} , it is known to correlate with the energy of the highest occupied molecular orbital (HOMO) for pentacene derivatives, but the effect is not completely understood.¹⁵ Indeed, the thienyl pentacene has an oxidation potential of 0.31 V (vs Fc/Fc^+),²⁰ compared to a potential of 0.10 V (vs Fc/Fc^+) for unsubstituted pentacene,¹⁵ which corresponds to an increased energy for the HOMO.

(19) The values reported in the text represent peak performance. Over a sample set of more than 10 devices from three independently manufactured substrates, the efficiency was $1.0 (\pm 0.2) \%$ with $J_{sc} = 4.0 \text{ mA/cm}^2 (\pm 1.1)$, $V_{oc} = 0.55 \text{ V} (\pm 0.06)$, and $FF = 0.46 (\pm 0.06)$.

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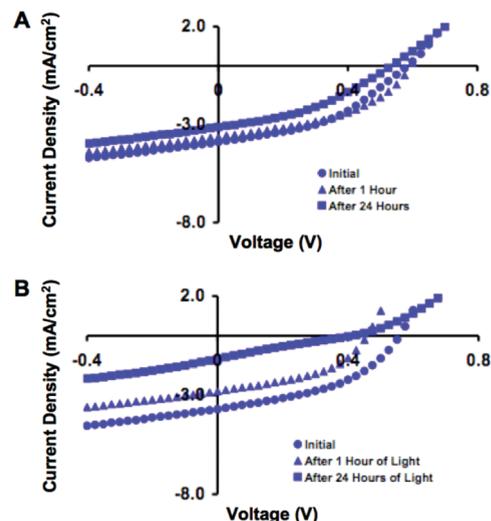


Figure 3. J - V curves for 6,13-di(2-thienyl)pentacene devices tested without constant illumination (A) and with constant illumination (B) at 100 mW/cm^2 . Representative initial curves are shown along with data for 1 h and 24 h of exposure to ambient atmosphere.

Although a number of processable pentacene derivatives also possess high open circuit voltages, they typically yield devices with relatively low J_{sc} values and, consequently, low efficiencies.¹⁵ What is the origin of the improved device performance for thienyl pentacene relative to these materials? Films of 6,13-di(2-thienyl)pentacene feature strong stacking, yielding a broadened absorbance with red-shifted maxima.^{1,20} Indeed, the normalized external quantum efficiency (EQE) spectrum (see the Supporting Information) is similar to the previously reported absorbance of thienyl pentacene thin films.¹ These spectra, coupled with the excellent carrier mobilities of $0.10 \text{ cm}^2/\text{V s}$ in amorphous films, may serve to explain the larger J_{sc} observed here relative to other solution processable pentacene derivatives.¹⁵

We recorded the evolution of the J - V characteristics of 6,13-di(2-thienyl)pentacene photovoltaics with and without constant illumination (Figure 3). In the absence of constant illumination, there is no change in device performance after 1 h (Figure 3A), and after 10 h of repeated testing, there is only a slight efficiency decay (see the Supporting Information). Note that over the same time period and in the absence of constant illumination, unencapsulated devices from unsubstituted pentacene decay completely.¹³

Under constant illumination, the situation is different. The device efficiency decays by $\sim 36\%$ after 1 h (Figure 3B), which is comparable to the degradation seen after 24 h of air exposure without constant illumination (Figure 3A). The important point is that even after 24 h of constant illumination, the devices continue to function (Figure 3B). This is a significant improvement over other pentacene-based devices, which have lifetimes of minutes in air.¹⁴

To assess long-term device stability, we compared device performance before and after storage in an inert atmosphere. Devices were tested, exposed to air for 24 h, and moved to a nitrogen glovebox. After 2 months of

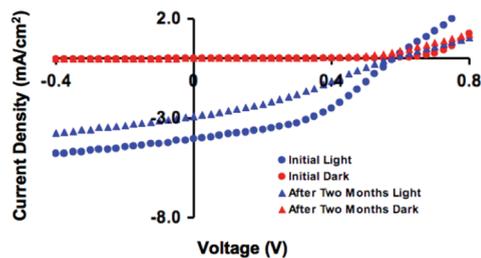


Figure 4. J - V curves with illumination (blue) and without illumination (red) for a 6,13-di(2-thienyl)pentacene device tested immediately after fabrication and after 2 months of storage.

storage, there was a less than a 50% decrease in efficiency (Figure 4). This indicates that the majority of the decay took place during initial testing/air exposure and further underscores the overall stability of 6,13-di(2-thienyl)pentacene-based devices.

Although there are changes in the V_{oc} and the FF after device operation (especially under constant illumination), the main source of device degradation appears to be a steady decrease in the J_{sc} (see the Supporting Information). Consequently, the stability of thienyl pentacene relative to unsubstituted pentacene can be rationalized as follows: because of the formation of oxygen adducts, devices from unsubstituted pentacene exhibit rapid degradation in air. However, for the 6,13-di(2-thienyl)pentacene, the thienyl substituent groups slow the rate of oxidation,^{1,20} greatly improving overall device lifetime both during ambient operation and long-term storage.

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In conclusion, the devices reported feature similar efficiencies and improved stability relative to other pentacene photovoltaics in ambient atmosphere. Notably, the device structure utilized here lacks low work function cathodes, can be processed in a simple fashion in air, and requires no encapsulation to achieve improved air stability. Here, instead of engineering the device structure, we have slowed typical degradation pathways and enhanced device stability by utilizing an air stable pentacene derivative. This approach holds great potential for the development of both efficient and air-stable organic photovoltaic devices that utilize a bulk heterojunction architecture.^{21–23}

Supporting Information Available: Typical atomic force microscopy image of a 6,13-di(2-thienyl)pentacene film; normalized external quantum efficiency spectra of a 6,13-di(2-thienyl)pentacene device; evolution of the efficiency and short circuit current for a device repeatedly tested over a period of 10 h (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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