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Bulk heterojunction organic photovoltaic devices based on phenyl-cored thiophene dendrimers

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(Received 17 April 2006; accepted 29 June 2006; published online 8 September 2006)

Bulk heterojunction organic photovoltaic devices have been fabricated by blending phenyl-cored thiophene dendrimers with a fullerene derivative. A power conversion efficiency of 1.3% under simulated AM1.5 illumination is obtained for a four-arm dendrimer, despite its large optical band gap of 2.1 eV. The devices exhibit an increase in short-circuit current and power conversion efficiency as the length of the arm is increased. The fill factors of the devices studied are characteristically low, which is attributed to overly uniform mixing of the blend. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337859]

Organic photovoltaic (OPV) devices offer an intrinsically low-cost, scalable approach to photovoltaic technology.¹ The bulk heterojunction device based on a π -conjugated polymer blended with a fullerene has been one of the most successful to date.² Solar power conversion efficiencies of such devices have improved over the last several years, and an efficiency of 4.8% has been certified at the National Renewable Energy Laboratory (NREL) for a polymer-fullerene OPV device.³ One of the salient features of bulk heterojunction devices is their sensitivity to the morphology of the blend.^{4,5} Crystalline ordering for both components on length scales of several nanometers has been shown to be beneficial to carrier transport and device efficiency.^{6,7} Thus, when choosing a material for use in OPV applications, the material's tendency to self-order is an important criterion.

Dendrimers constitute an intriguing class of molecules⁸ that has arisen for use in organic optoelectronic applications. Π -conjugated dendrimers have proven to be efficient charge transporters in organic light emitting diodes, which was attributed to the high-quality films formed by the dendrimers.⁹ Due to strong cofacial π - π interactions, these molecules can show a high degree of molecular ordering. The film morphology of dendrimers is aided by their monodisperse nature, which provides a potential advantage over polymers. Polymers can be difficult to synthesize with a low degree of polydispersity. This is problematic for device development because the carrier mobility of polymers can depend strongly on their molecular weight.^{10,11} Dendrimers are also easily purified to a high degree using simple techniques such as column chromatography. Taken together, the above attributes make dendrimers well suited for studying structure-property relationships in organic semiconductors, and they are potential candidates as light-absorbing and charge-transporting agents in efficient OPV devices. Here we demonstrate the use of phenyl-cored thiophene dendrimers in bulk heterojunction OPV devices fabricated by blending them with [6,6]-phenyl C60 butyric acid methyl ester (PCBM).

We have previously synthesized and characterized a family of dendrimers with phenyl cores and thiophene dendrons (arms).¹² Use of thiophenes was motivated by the success of polythiophenes in OPV devices due to their relatively low optical band gap and high charge carrier mobility.^{7,13} Additionally, thiophene chemistry is generally well understood, and the synthesis of thiophene-based dendrimers has previously been demonstrated.¹⁴ The family of dendrimers discussed here possesses optical band gaps ranging from 2.10 to 2.55 eV, making them poor solar absorbers. However, this family of thiophene-based dendrimers makes a good test bed for investigating the general feasibility of using dendrimers in OPV devices.

The dendrimers used in this study are described in Fig. 1. They are coded *mGp-nS*, where *m* denotes the number of dendrons (arms) around the phenyl core (3 or 4), *p* is the generation, or degree of branching, of the dendrons (1 or 2), and *n* is the number of thiophene units in the bridge between the core and the first branching point of the dendron (from 1 to 3). The only second-generation dendrimer used in this study was one with three arms around the core and one

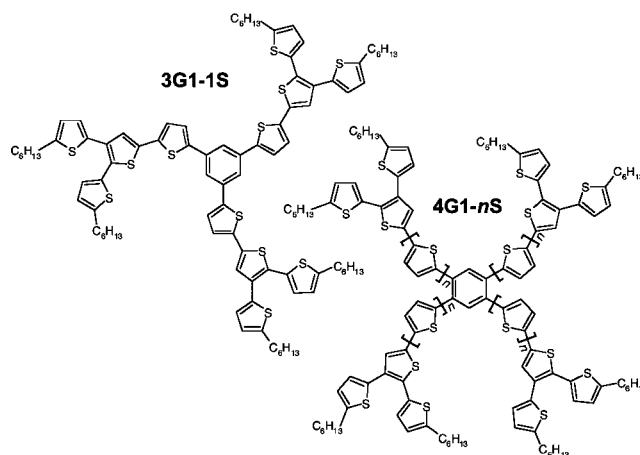


FIG. 1. Molecular structures of the dendrimers used in this study. First generation dendrimers with three or four dendrons around the core (3G1-1S and 4G1-*nS*, respectively) were used, and the number of thiophene units in the dendron bridge of 4G1-*nS* was varied between *n*=1 and *n*=3. A second-generation dendrimer with three dendrons around the core and one thiophene in the bridge (3G2-1S) was also used but is not shown.

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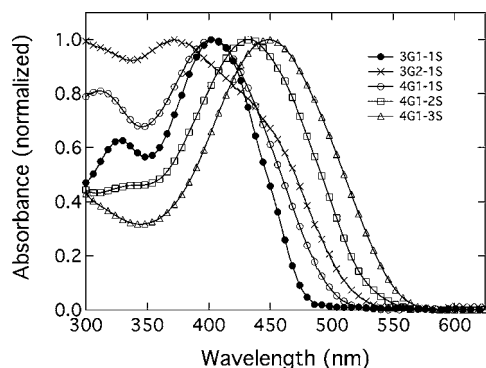


FIG. 2. Optical absorption spectra of thin films of the dendrimers 3G1-1S (closed circles), 3G2-1S (crosses), and 4G1- n S ($n=1$ open circles, $n=2$ squares, and $n=3$ triangles).

thiophene unit in the bridge, 3G2-1S. The synthesis and characterization of the *mGp*-1S dendrimers used in this study have been previously reported.¹² The dendrimers 3G2-1S, 4G1-2S, and 4G1-3S were prepared in a similar manner, but with the addition of the bridging thiophene moiety added to the dendron via Stille coupling before uniting the dendron and the core in the final synthetic step. Dendrimers 3G1-2S and 3G1-3S were also synthesized, but they proved to be too insoluble for device studies.

Thin films of the dendrimers were prepared for optical absorption measurements from a 20 mg/ml toluene solution by spin coating onto quartz substrates at 1000 rpm. For use as the active layer in bulk heterojunction photovoltaic devices, the dendrimers were blended with [6,6]-phenyl C60 butyric acid methyl ester (PCBM) in a 1:1 (by volume) mixture of toluene:chlorobenzene. The weight ratio of dendrimer to PCBM was 1:2, but in the case of 4G1-3S the ratio was varied from 1:1 to 1:4. For an initial study comparing the device performance across the family of dendrimers, the total concentration of dendrimer and PCBM in solution was kept constant at 30 mg/ml. The active layer blend was spin coated onto a patterned indium tin oxide substrate coated with ~ 80 nm of Baytron P VP AI 4083 (H.C. Starck Inc.), which had been annealed on the hotplate at 120 °C for 10 min. For the initial study, the thickness of the active layer was approximately 130 nm. For fabrication of an improved device based on 4G1-3S, a total concentration of 20 mg/ml was used, resulting in an active layer thickness of 100 nm. Al top contacts (80–100 nm) were thermally evaporated in high vacuum through a shadow mask to form devices with active area of 0.1 cm². The completed devices were annealed at 90 °C for 10 min on a hotplate. Active layer deposition, annealing, and device characterization were performed in argon atmosphere. Photovoltaic device performance was characterized using the user-facility Spectrolab XT-10 solar simulator at NREL. The intensity of the simulator was nominally set to 100 mW/cm² using a reference Si solar cell. After the measurements, the resulting power conversion efficiencies were corrected for spectral mismatch. External quantum efficiency spectra were measured by illuminating the device with low-intensity monochromatic light. Tapping-mode atomic force microscopy (AFM) was performed with Digital Instruments NanoScope IV.

Optical absorption spectra of thin films of the dendrimers are shown in Fig. 2. Optical band gaps of the dendrimer films were estimated from the low energy onset of the absorption and are listed in Table I. As discussed in detail

TABLE I. Summary of the thin film optical band gap E_G of the dendrimers and the J_{SC} , V_{OC} , fill factor FF, and efficiency η of the dendrimer:PCBM devices under AM1.5 illumination.

Active layer (weight ratio)	E_G (eV)	J_{SC} (mA/cm ²)	V_{OC} (mV)	FF (%)	η (%)
3G1-1S:PCBM (1:2)	2.55	0.64	910	25	0.17
3G2-1S:PCBM (1:2)	2.28	0.96	803	26	0.21
4G1-1S:PCBM (1:2)	2.34	0.21	870	26	0.05
4G1-2S:PCBM (1:2)	2.15	0.68	776	27	0.14
4G1-3S:PCBM (1:2)	2.10	1.65	868	33	0.48
4G1-3S:PCBM (1:1)	2.10	0.62	864	28	0.14
4G1-3S:PCBM (1:3)	2.10	1.86	865	34	0.55
4G1-3S:PCBM (1:4)	2.10	1.93	864	33	0.57

elsewhere,¹² the optical band gap of the dendrimer is correlated to the degree of conjugation in the molecules. Due to the meta-coupling, the three-arm dendrimers are not as conjugated as the four-arm dendrimers. However, the four-arm dendrimers suffer from twisting due to steric interactions, limiting the expected lowering of their band gap. Increasing the number of thiophenes in the bridge of the 4G dendrimers to yield 4G1-2S and 4G1-3S, or adding a second generation to the 3G1-1S to yield 3G2-1S, decreases the optical band gap, as expected due to the increased conjugation length. The dendrimer with the lowest optical band gap (2.10 eV) used in this study was 4G1-3S.

A summary of the performance of the photovoltaic devices from the initial study comparing the different dendrimers, as well as investigating the dendrimer to fullerene ratio, is listed in Table I. The trends in the performance of the devices can be correlated to the measured band gaps of the dendrimers as well as their anticipated molecular conformations. For a dendrimer to fullerene ratio of 1:2, 3G2-1S is seen to have an increased short-circuit current (J_{SC}) and decreased open-circuit voltage (V_{OC}) relative to 3G1-1S, as would be expected from a decrease in band gap. 3G1-1S is seen to have increased J_{SC} relative to 4G1-1S despite the smaller band gap for 4G1-1S. We attribute this to better π stacking of the three-arm dendrimer. We have already reported that the geometry of the three-arm dendrimers is more planar than that of the four-arm ones.¹² A more planar geometry would favor π -stacking of the molecules and would enhance the charge transport properties, in agreement with the observed higher J_{SC} for 3G1-1S. Examination of the impact of the length of the dendron reveals a systematic increase in J_{SC} from 0.21 to 1.65 mA/cm² in going from 4G1-1S to 4G1-3S. This increase is far greater than expected from the decrease in band gap, which we calculate to result in approximately a 60% increase in J_{SC} from 4G1-1S to 4G1-3S as a result of better overlap with the AM1.5 spectrum. An additional factor that contributes to the improvement of the devices is an increase in the hole mobility as the arm is lengthened. Preliminary transport measurements using time-resolved microwave conductivity (TRMC),¹⁵ which will be reported in detail elsewhere, indicate that the lower limit of the mobility of charge carriers increases from 1.6×10^{-5} cm²/V s in 4G1-1S to 4.7×10^{-5} cm²/V s in 4G1-2S and to 2.3×10^{-4} cm²/V s in 4G1-3S. For comparison, the lower limit of the charge carrier mobility in poly-3-hexylthiophene (P3HT), measured with the same technique, has been reported as 2×10^{-4} cm²/V s.¹⁵ Due to the similar-

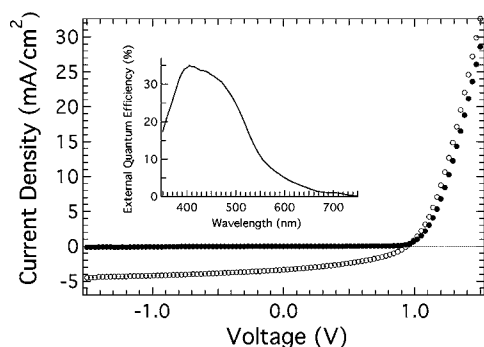


FIG. 3. J - V curve of the improved 4G1-3S:PCBM (1:4) device under simulated AM1.5 illumination (solid) and in the dark (dashed). The inset is the external quantum efficiency vs wavelength of the device.

ity between P3HT and the thiophene dendrimers, we assume that the scaling factor for the conversion of the lower limit to actual carrier mobility is similar. We therefore conclude that (a) there is a systematic increase in charge carrier mobility as the length of the arm increases and (b) the 4G1-3S dendrimer used in the best device reported here has a charge carrier mobility that is very similar to that of P3HT with a value of $0.014 \text{ cm}^2/\text{V s}$ as measured by TRMC.¹⁵

Finally, a study on the weight ratio of 4G1-3S to fullerene demonstrated a systematic increase in J_{SC} in going from 1:1 to 1:4. This would indicate that higher fullerene contents are required with this donor-acceptor system to achieve good phase separation of the materials, which is necessary to reduce carrier recombination.¹⁶

Based on the above findings, an improved device was fabricated using a 4G1-3S:PCBM (1:4) blend. Reducing the active layer thickness to approximately 100 nm was found to substantially increase the performance of the device, resulting in J_{SC} , V_{OC} , fill factor, and efficiency of $3.35 \text{ mA}/\text{cm}^2$, 940 mV, 40%, and 1.3%, respectively. The J - V curve for this improved device is shown in Fig. 3. The external quantum efficiency of this device, shown in the inset to Fig. 3, exhibits a maximum of 35% at a peak wavelength of 405 nm with a broad peak extending out to approximately 500 nm. AFM imaging of this active layer film, shown in Fig. 4, revealed relatively small-scale phase separation of the dendrimer and PCBM components with domain sizes of less than 10 nm. Such a fine blending of the donor and acceptor components in a bulk heterojunction can result in increased carrier recombination, which would adversely affect device performance. We therefore attribute the low fill factor of these dendrimer devices, and the performance enhancement seen upon reducing the active layer thickness, to the extremely fine blending of the two components. Work on improving this morphology is in progress.

In conclusion, photovoltaic devices have been fabricated by blending a family of phenyl-cored thiophene dendrimers with PCBM. The device performance indicates that the three-arm dendrimer in this family has better charge transport than the analogous four-arm dendrimer. Increasing the length of the dendron in the four-arm dendrimer resulted in a systematic increase in device performance, which we attribute to increased carrier mobility. Poor solubility of the three-arm dendrimers with longer dendrons prevented investigation of photovoltaic properties. The best device used the 4G1-3S dendrimer and exhibited a peak external quantum efficiency of 35% and an AM1.5 power conversion effi-

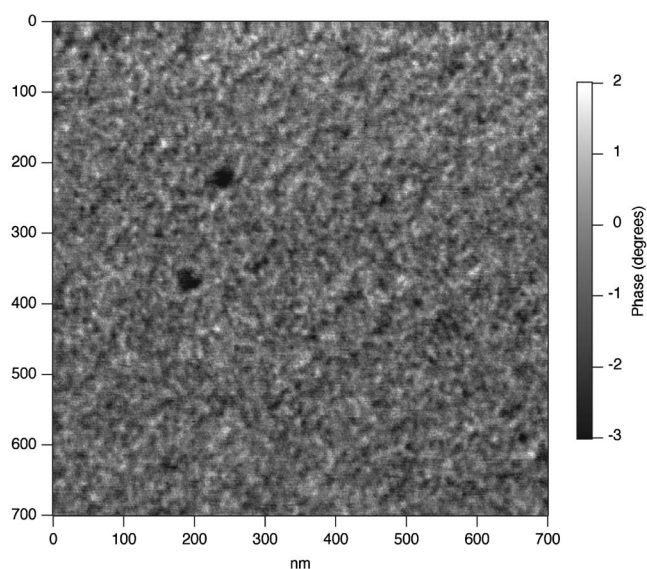


FIG. 4. Tapping-mode AFM phase image of the surface of the 4G1-3S:PCBM (1:4) film.

ciency of 1.3% (Fig. 3). The low fill factor and small-domain morphology of these devices indicate that carrier recombination is probably a limiting factor in their performance. Given the large optical band gaps of the dendrimers studied here, the obtained efficiencies demonstrate that dendrimers are promising as light absorbers and charge transporters in organic photovoltaic devices. Efforts to decrease the band gap of these materials are underway.

The authors gratefully acknowledge support for the research on organic photovoltaics from the NREL DDRD program and from the Xcel Energy Renewable Development Fund. Research at NREL is carried out under DOE Contract No. DE-AC36-99-GO10337.

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