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ABSTRACT

A family of prototype π -conjugated dendrimers has been synthesized and incorporated into solution-processable organic photovoltaic (OPV) devices. Bulk heterojunction devices were fabricated by blending the dendrimers with a solubilized fullerene. The best of these initial devices, which were not optimized for morphology, exhibited external quantum efficiencies of 22% at peak wavelength. It was found that 3-arm dendrimers, when sufficiently soluble, yielded higher photocurrents than their 4-arm counterparts. This was attributed to better planarity and intermolecular alignment of the 3-arm version. Device efficiency was seen to increase with increasing arm length. A reduced-band gap dendrimer was synthesized by attaching electron-withdrawing groups onto the core to yield an optical band gap of 1.82 eV.

1. Objectives

Polymer-based OPV offers the promise of low-cost, solution-based solar cell fabrication that can be readily scaled up to large areas.¹ Efficiencies up to 4.8% have been verified at NREL for research-scale OPV devices based on bulk heterojunction polymer-fullerene blends.²⁻⁴ Extraction of charge carriers from the active layer in these devices has been shown to be critically dependent upon the molecular morphology,⁵ which in turn is impacted by the molecular weight distribution of the polymer.⁶ We are investigating the use of dendrimers as a substitute for the polymer in such devices. Dendrimers possess a monodisperse molecular weight distribution that allow for a high degree of molecular ordering and thus high carrier mobilities. Additionally, dendrimers can be easily purified using column chromatography techniques.

Here we report our initial attempts at fabricating OPV devices using dendrimers. We have synthesized a family of dendrimers consisting of thiophene-based dendrons (arms) attached to a phenyl core.⁷ This family provides a test best for studying the structure-property relations of these novel materials.

2. Technical Approach

The dendrimers used in this study (Fig. 1) consisted of a phenyl core with either three or four pendant dendrons. The dendrons contained between one and three thiophene moieties in a linear chain leading to a branching point. The generation of the dendrimer is defined as the number of levels of branching. The nomenclature used for a particular dendrimer in this study is " $mGp-nS$ ", where m is the number of dendrons, p is generation number, and n is the

number of thiophenes in each arm. The dendrimers were synthesized with a convergent method where the cores and dendrons were prepared separately and then united in the final step. Stille coupling was used to bond the cores to stannane-functionalized dendrons. A reduced-band gap dendrimer, 3G1-2S-CN, was obtained by adding electron-withdrawing CN groups to the positions on the phenyl core that were not occupied by dendrons. Also, an acetylene group was inserted between the core and the dendron to alleviate twisting of the backbone. 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) 1:2 by weight. In the case of 4G1-3S the ratio was varied from 1:1 to 1:4.

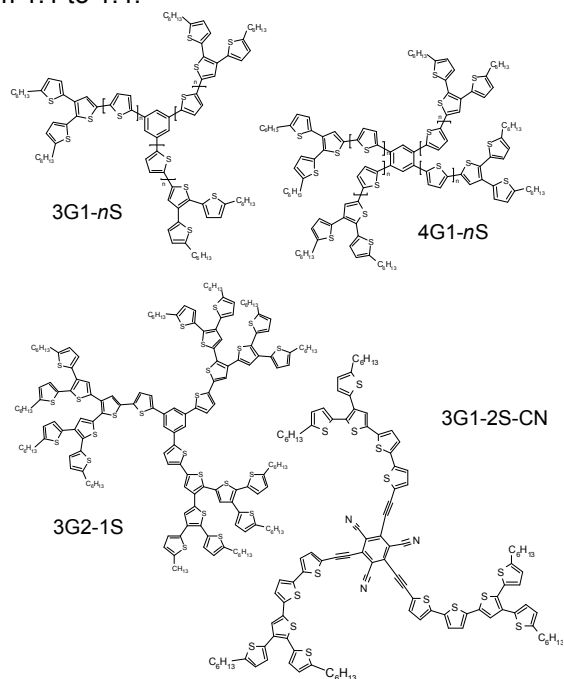


Fig. 1. Structures of the dendrimers used in this study.

3. Results and Accomplishments

3.1 Dendrimer Characterization

Optical absorption spectra of thin films of the dendrimers are shown in Fig. 2. The absorption is seen to systematically push to the red as the number of thiophenes in the dendron is increased. A modest red shift is also seen for 4-arm versus respective 3-arm dendrimers. This is expected from the increased π -conjugation for dendrons connected through ortho positions versus meta positions. That the red shift is not stronger is attributed to steric hindrance of the bulky dendrons that induce twisting out of the plane of the core. A large red shift is seen in 3G1-2S-CN owing

to the incorporation of the –CN group onto the core. A fit to the low energy tail of the absorption, assuming an Urbach edge, yielded an optical band gap of 1.82 eV.

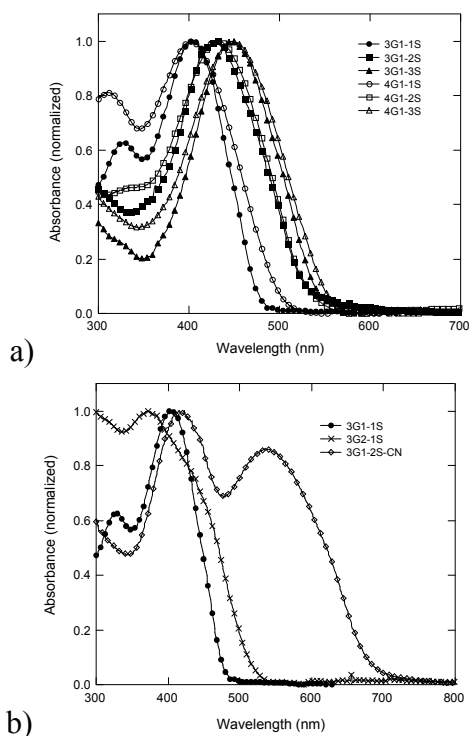


Fig. 2. Optical absorption spectra of the dendrimers illustrating the effects of a) the dendron length and the number of arms and b) a second generation 3G2-1S and the CN-pendant core version 3G1-2S-CN.

3.2 Preliminary Carrier Transport Measurements

Initial time-resolved microwave conductivity measurements (TRMC) were carried out by collaborators at the University of Delft. For 4G1-3S, carriers created by pulsed radiolysis showed a power-law dependence of lifetimes extending into the millisecond regime, indicative of a very pure organic semiconductor. Fits to a 1-D transport model yielded a mobility (electron plus hole) of $0.8 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, a value similar to that found for discotic liquid crystals.

3.3 Bulk Heterojunction Device Results

Table 1 shows the OPV device performance for the dendrimers, excluding 3G1-2S and 3G1-3S, which were insufficiently soluble, and 3G1-2S-CN, which has yet to be characterized. 3G1-1S is seen to yield 3x times the photocurrent of 4G1-1S. From this we conclude that 3G1-1S has better molecular ordering and transport characteristics. Preliminary computational models show that 4G1-1S is less planar. For both the 3G and 4G dendrimers the photocurrent increases with increasing number of thiophenes in the dendron. We attribute this to better planarity of the molecule as the arms become longer and thus push the bulky end groups further from the core, as well as a small contribution from the decrease

in band gap with longer arms. The optimal blending ratio between 4G1-3S and fullerene was found to be 1:4. This indicates that significant amounts of fullerene loading are necessary to yield clear phase segregation in this blend. For the best device tested here, 4G1-3S/PCBM, the external quantum efficiency was found to be 22% at a peak wavelength of 460 nm.

Table 1. Summary of device performance. Device structure: ITO/PEDOT:PSS/Active Layer/Al

Active Layer, PCBM Weight Ratio	J_{sc} (mA/c m ²)	V_{oc} (mV)	FF (%)	η (%)
3G1-1S, 1:2	0.64	910	25	0.15
3G2-1S, 1:2	0.96	803	25.9	0.20
4G1-1S, 1:2	0.21	870	26	0.05
4G1-2S, 1:2	0.68	776	27	0.14
4G1-3S, 1:2	1.65	868	32.9	0.47
4G1-3S, 1:1	0.62	864	28	0.14
4G1-3S, 1:3	1.86	865	33.5	0.54
4G1-3S, 1:4	1.93	864	33.1	0.56

4. Conclusions

Prototype OPV devices have been fabricated using dendrimers. A peak external quantum efficiency of 22% was obtained, a promising result for non-optimized devices. Open circuit voltage of approximately 0.9 V was seen for most of the materials. This initial set of dendrimers, although possessing large optical band gaps and thus not ideally suited as solar absorbers, demonstrated the feasibility of replacing polymers with dendrimers in bulk heterojunction devices. A reduction in band gap to 1.82 eV was demonstrated with the introduction of electron-withdrawing groups onto the dendrimer core.

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