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High Efficiency Organic Photovoltaics Incorporating a New Family of Soluble Fullerene Derivatives

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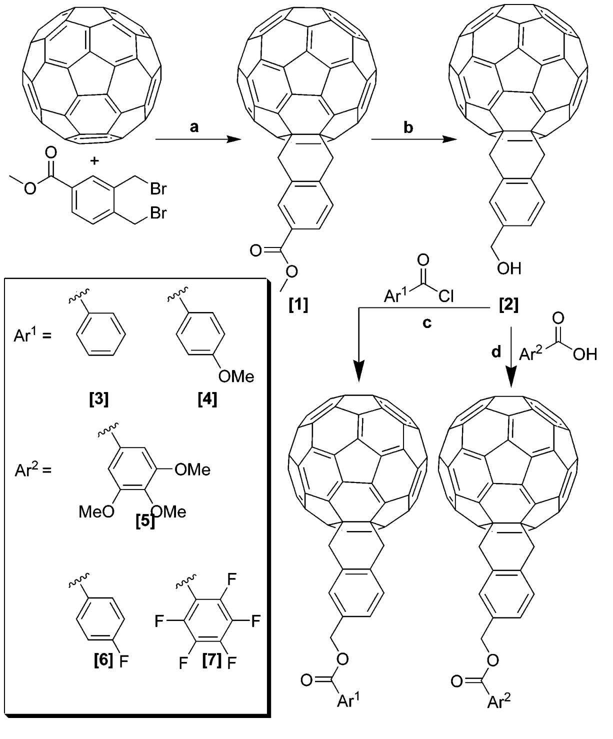
Buckminsterfullerene (C$_{60}$) has proven to be an invaluable electron conducting (n-type) semiconductor for organic electronics.[1] However, its minimal solubility in organic solvents necessitates derivatization to take advantage of inexpensive solution-based processing techniques. There are several reaction pathways commonly used to functionalize C$_{60}$ with solublizing moieties;[2−4] however, research efforts in solution-processed organic electronics are dominated by the use of one derivative in particular: [6,6]-phenyl-C$_{61}$ butyric acid methyl ester (PCBM).[5,6]

PCBM is most commonly used when blended with a light-absorbing and hole-conducting conjugated polymer to afford the bulk-heterojunction active layer in a photovoltaic device.[7] Several research groups have reported that such solution-processed organic photovoltaics (OPVs) can achieve power conversion efficiencies (PCEs) under standard illumination conditions (AM 1.5 G, 80−100 mW/cm^2) in the 2−3% range with poly(phenylene vinylene) (PPV) based materials[8] and 4−5% range with poly(3-hexylthiophene) (P3HT),[9−12] representing the most efficient OPVs reported to date. As such, strong inquiry has arisen into the structural basis for the high performance of polymer/PCBM photovoltaics.

While PCBM remains the best performing soluble fullerene derivative, it is not necessarily the optimum structure for solution processed OPVs. Attempts have been made to develop new fullerenoids for OPVs by attaching solublizing groups to C$_{60}$ using varying strategies. This has led to the development of C$_{60}$ derivatives including PCBM analogues with altered substitution patterns on the solubilizing phenyl ring[13] or replacement of the phenyl ring altogether with a thiophenyl ring.[14] Other structures have been based on diphenyl C$_{61}$ and dicarboxy C$_{61}$ groups.[15−17] Replacement of the methano bridge present in both PCBM and many other derivatives with an alternate attachment allows for the study of new classes of fullerenoids. Reported here is the synthesis and evaluation of a new highly soluble family of dihydronaphthyl bridged ester derivatives which, given their high device performance, identifies a new effective solublization strategy for fullerenes in OPVs.

Scheme 1. Synthesis of a Family of Soluble Fullerene Derivatives[a]



[a] Conditions: (a) KI, 18-C-6, PhMe, reflux 10 h, 36%; (b) DIBAL, DCM, 0 °C then rt 2 h, 73%; (c) DMAP, TEA, DCM, rt 8 h, 87% [**3**], 76% [**4**]; and (d) DMAP, DCC, DCM, rt 8 h, 93% [**5**], 81% [**6**], and 96% [**7**].

The route to the family of dihydronaphthyl derivatives is shown in Scheme 1. Methyl ester **1** is a moderately soluble fullerene derivative previously synthesized in two steps, the intermediate product being a highly insoluble carboxyfullerene.[18] Here, compound **1** was synthesized by the direct reaction of C$_{60}$-fullerene with an ortho-dimethinequinine

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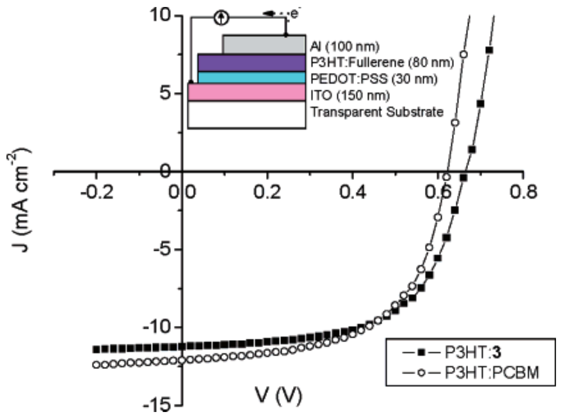

Figure 1. *J*−*V* curves representing best device performance for P3HT/**3** and P3HT/PCBM bulk heterojunction solar cells. Inset is a schematic of device architecture with approximate layer thicknesses.

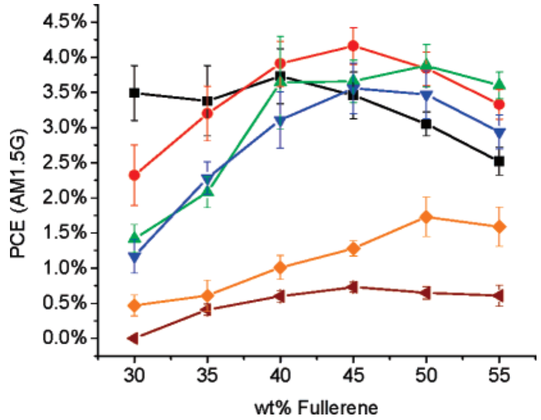

Figure 2. Average PCEs (eight devices) with **3** (●), **4** (▲), **5** (◆), **6** (▼), **7** (solid left-pointing triangle), or PCBM (■) as a function of weight percent in P3HT. The performance of devices made with compound **3** was consistant and reproducable with an average $V_{OC} = 650$ mV, $J_{SC} = 11.3$ mA cm^{-2}, and a fill factor of 57%, for an average PCE of 4.2% at 45 wt % fullerene. The error bars represent the 95% confidence interval.

formed in situ by reaction of methyl-(3,4-dibromomethyl)-benzoate with potassium iodide. The benzyl alcohol, **2**, was synthesized from the ester via reduction with diisobutylaluminum hydride. This alcohol is sufficiently soluble in common organic solvents (tetrahydrofuran, dichloromethane (DCM), and chloroform) to represent a highly useful synthon for the development of fullerene based materials; the functional handle is easily elaborated upon via esterification to give soluble fullerenoids as seen in Scheme 1. Esterification of compound **2** with benzoyl chloride and subsequent purification following published procedures[17] afforded compound **3**, a dihydronaphthyl fullerene benzyl alcohol benzoic acid ester. To more fully explore this solubilizing group architecture, a range of electron rich and poor benzoic acid ester derivatives of **2** were synthesized to give compounds **4**−**7**, which, along with **3**, are all sufficiently soluble in organic solvents (>30 mg/mL) to make incorporation into solution cast device formulations possible.

To evaluate the performance of these new fullerenoids, spin-cast bulk heterojuction active layer OPVs were fabricated with P3HT (Rieke Metals, Inc.). Photovoltaic devices consisted of a standard ITO/PEDOT:PSS/P3HT:fullerene/Al architecture (see inset of Figure 1).[9] Completed devices were annealed at 150 °C for 30 min and tested under argon using a solar spectrum simulator at AM 1.5 G and a spectrally matched intensity of 100 mW/cm^2.

Because bulk heterojunction OPV performance is known to be a strong function of donor/acceptor ratio,[9,11] a series of devices were fabricated using each new fullerene derivative or PCBM by altering the P3HT/fullerene ratio. The top performing fullerene derivative was found to be the fullerene derivative **3** with an optimal composition of 45 wt % fullerene. Figure 1 shows the best *J*−*V* curves for devices made with either PCBM or **3** at 40 wt % and 45 wt % fullerene, respectively. The curves represent PCEs of 4.5% for **3** and 4.4% for PCBM. The performance of **3** matches or slightly exceeds that of PCBM in our experiments and is comparable with reports for the top P3HT/fullerene OPVs.[9−12]

The other fullerene derivatives showed varied performance in OPVs as shown in Figure 2 where the average performance of devices fabricated with each derivative is plotted against the fullerene weight %. The dihydronaphthyl fullerene benzyl alcohol 4-methoxybenzoic acid ester **4** and the dihydronaphthyl fullerene benzyl alcohol 4-fluorobenzoic acid ester **6** also performed impressively with moderate decreases in PCE as compared to **3**, which are due primarily to a marked decrease in the fill factor, as the voltages and currents are comparable. The significantly lower performance of the remaining derivatives, dihydronaphthyl fullerene benzyl alcohol 2,3,4-trimethoxybenzoic acid ester **5** and dihydronaphthyl fullerene benzyl alcohol pentafluorobenzoic acid ester **7**, is due to lower values for both J_{SC} and V_{OC}. Devices made with **7** also showed a lower fill factor than the other compounds at each of the compositions tested. Overall, the derivatives containing phenyl rings with significantly altered electron density demonstrated the lowest performance.

To probe the basis for this substituent effect, the electrochemical properties of each derivative were analyzed by cyclic voltammetry. The reduction onsets for the new fullerenoids were all found to be essentially identical with a small variation (<0.1 V), suggesting that there is little difference in the LUMO levels of the fullerenes. In addition, no trend in average V_{OC} values for devices at 45 wt % fullerene (ranging from 0.43 V to 0.65 V) with respect to electronegativity of the solubilizing group is observed. This suggests that the electron density of the phenyl group of compounds **3**−**7** has no direct effect on the electronic characteristics of the fullerenoid and is in contrast to trends seen for PCBM derivatives with similar substitution patterns on the phenyl ring.[14] It is likely that the relative placement of the ring decreases any intramolecular effect between the solublizing ring and the fullerene. However, the changes in phenyl ring electron density may affect the intermolecular interactions in the solid state.[14,19]

Polymer/fullerene mixing and the formation of an interpenetrating bulk heterojunction have an effect on OPV performance and are dependent on material properties; the structure of the fullerenoid and its interaction with the conjugated polymer are important factors.[19−21] The PCEs for

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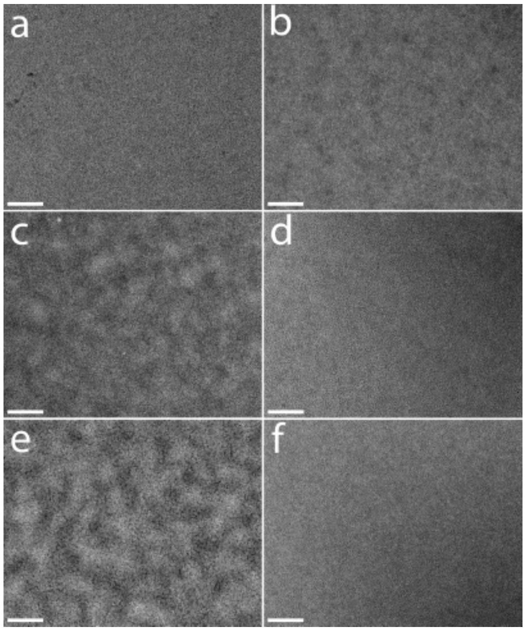

Figure 3. Transmission electron micrographs of annealed films (30 min, 150 °C) composed of blends of P3HT and 45 wt % (a) PCBM, (b) **3**, (c) **4**, (d) **6**, (e) **5**, and (f) **7**. Scale bars are 500 nm.

the three top performing fullerene derivatives all show optimum P3HT/fullerene ratios of 45 or 50 wt % in contrast to PCBM, where the optimum was 40 wt %. In addition, the PCEs of devices made with PCBM demonstrate a weaker dependence on wt % of fullerene, especially at lower wt %. This indicates a possible difference in polymer/fullerene miscibility in a bulk heterojunction thin film. To evaluate such morphological differences, studies were performed on thin film blends of P3HT and each of the fullerenoids using previously reported methods.[22] Transmission electron microscopy (TEM) micrographs (Figure 3) of the thin films show that, after annealing, there is a slight difference between films of P3HT/PCBM and films of P3HT/**3**; domains appearing darker in the TEM images are visible on the 200−500 nm length scale. These are presumably areas of increased fullerene concentration due to aggregation.[23] In comparing films containing the substituted benzoate derivatives, the degree of phase segregation increases with the addition of electron-rich solublizing groups. Where films containing the fluorinated benzoates (**6** and **7**) are relatively homogeneous by TEM, the methoxy (**4**) and trimethoxy (**5**) blends show successive increases in the phase segregation as compared to P3HT/**3** films. The degree of phase segregation is not catastrophic, as large scale crystallization of the fullerene does not occur. A possible origin of this decrease in compatibility may be a lower degree of electronic attraction between the electron-rich methoxy benzoates and the thiophenyl rings of the P3HT polymer matrix. While no direct correlation between the differences in electronic and morphological properties and device performance is readily apparent, further work in identifying such structure−property relationships is ongoing.

In conclusion, we have successfully synthesized both a novel fullerenoid benzyl alcohol as well as a highly soluble family of fullerene benzoates. The dihydronaphthyl fullerene benzyl alcohol is a soluble, functional fullerene derivative able to be used as a core for further elaboration via esterification. Initial characterization and device testing indicate that esters synthesized from the parent benzyl alcohol are suitable for use in bulk heterojunction solar cells. Devices fabricated with the new dihydronaphthyl fullerene benzyl alcohol benzoic acid ester (**3**) exhibit PCEs of up to 4.5% under standard illumination conditions. This represents the highest reported PCE for a non-PCBM based polymer/fullerene solar cell and suggests that excellent alternatives to PCBM may yet be found.

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Supporting Information Available: Further information on experimental details, characterization, and complete device fabrication conditions are reported (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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