This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Facile Synthesis and Photovoltaic Applications of a New Alkylated Bismethano Fullerenes as Electron Acceptor for High Open Circuit Voltage Solar Cells

Derya Baran, Sule Erten-Ela, Andreas Kratzer, Tayebeh Ameri, Christoph Brabec, Andreas Hirsch

Received (in XXX, XXX) Xth XXXXX 20XX, Accepted Xth XXXXX 20XX
DOI: 10.1039/b000000x

It is crucial to control the lowest unoccupied molecular orbital (LUMO) of electron accepting materials for producing efficient charge transfer in bulk heterojunction (BHJ) solar cells. Due to their high LUMO level, soluble bis-adducts of C₆₀ are of high interest for improving the Vₜₜ of BHJ solar cells. In this work, we have developed a novel bis-4-propylpentyl [6,6] methanofullerene bis-adduct, NCBA, using an alkyl solubilizing group. The optoelectronic, electrochemical and photovoltaic properties of this bis-product are investigated. NCBA is successfully applied as the electron acceptor with poly(3-hexylthiophene) (P3HT) in BHJ solar cell showing a high Vₜₜ of 0.73 V.

Introduction

The power conversion efficiencies of organic photovoltaic devices have been swiftly increased in the last years to 11% for single junction polymer: fullerene cells. Poly(3-hexylthiophene) (P3HT) is the widely used commercial conjugated polymer donor material, and [6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) is the most important soluble C₆₀ derivative as an acceptor in BHJ solar cells. Power conversion efficiencies (PCE) around 4-5% has been reached based on the P3HT/PCBM system by device optimization. The PCE of the bulk heterojunction solar cells has been steadily increased by research progress on both the new photovoltaic materials and new device structures. Molecular design of the photovoltaic materials will play a key role in promoting the commercial application of the bulk heterojunction solar cells. In order to further improve the PCE of the polymer solar cells (PSCs), finding new conjugated polymer donor materials bearing broader absorption, lower bandgap, higher hole mobility, and suitable electronic energy levels have been the main goal in OPV field and some copolymers using push-pull property in the conjugated backbone showed higher photovoltaic efficiency than P3HT. Nevertheless, the research efforts toward new C₆₀ derivative acceptor materials to replace PCBM have not been very successful until now with different polymer donors.

Among fullerene derivatives, PCBM offers the advantages of good solubility in organic solvents (chloroform, chlorobenzene, dichlorobenzene, etc.), higher electron mobility and higher electron affinity. However, weak absorption in the visible region and low lying LUMO level are the weak points. Weak absorption of PCBM limits the light harvesting in photovoltaic conversion and low LUMO level of the acceptor result in lower open circuit voltage (Vₜₜ) in PSCs, since Vₜₜ is strongly related to the difference between the LUMO level of acceptor and the HOMO of the donor material. Therefore, it is very important to design and synthesize new soluble fullerene derivatives with stronger visible absorption and higher LUMO energy levels than PCBM. Although many C₆₀ derivatives and a new C₆₄ derivative have been synthesized and utilized as acceptors in OPVs, only handful C₆₀ derivatives achieved good solubility in organic solvents, desired electron mobility to have good charge transport, broad absorption to contribute to the photocurrent and suitable electronic levels to have efficient charge dissociation. The research effort devoted to new fullerene acceptor materials are increasing but the new fullerene derivative acceptors showing better photovoltaic performances than PCBM are very few. PCBM is still the most important acceptor material used in the organic solar cell studies. The miscibility and energy level match of fullerene acceptors with the low bandgap polymer donors should also be considered for achieving a high power conversion efficiency of organic solar cells.

Among these electron acceptors based on fullerene, fullerene bis-adducts, which have two solubilizing groups, effectively increase Vₜₜ compared to P3HT:PCBM blended systems. The fullerene bis-adducts have higher LUMO energy levels because of the reduction of the molecule’s electron affinity due to the presence of fewer unsaturated bonds as compared with fullerene monoadducts.
Blom et al. reported bis-PCBM (a regioisomeric bis-adduct of PCBM) used as an electron acceptor and the $V_{oc}$ of the P3HT:bis-PCBM BHJ solar cells was 0.05 V higher than that of P3HT:PCBM due to the higher LUMO energy level of bis-PCBM as compared to PCBM.\textsuperscript{26} Afterwards, Laird and Li et al.\textsuperscript{27,29,31} reported a remarkable bis-adduct fullerene derivative, indene-C$_{60}$ bis-adduct (ICBA). Through the Diels-Alder reaction of indene to C$_{60}$, ICBA achieves a LUMO energy level that is 0.17 eV higher than that of singly functionalized PCBM. A PSC consisting of P3HT and ICBA demonstrated a $V_{oc}$ of 0.84 V. However, due to byproducts, multistep purification procedures and the high cost of ICBA their future commercial application will be limited in PSCs.

Herein, we introduce a new soluble fullerene based n-type semiconductor material, bis-4-propylpentyl-[6,6]-methanofullerene (NCBA), using 4-nonanone as a building block. Compared to indene bis-adducts which requires a large excess of indene to produce the final product (mole ratio of indene to C$_{60}$=20:1), NCBA as shown in Scheme 1 is easily synthesized from of 4-nonyl-p-tosylhydrazone and C$_{60}$ using 2:1 mole ratio. The synthesis of 4 was carried out by 1,3-dipolar cycloaddition reaction of diazo compound generated in situ by reaction between tosylhydrazone and sodium methoxide (Scheme 1). Condensation of 1 with p-tosylhydrazide in toluene affords tosylhydrazone 3, which after sequential treatment with sodium methoxide in pyridine and C$_{60}$ in refluxing DCB affords bis-4-propylpentyl-[6,6]-methanofullerene (4) isomer mixture. Highly soluble bis-alkyl side chains raised the LUMO level 70 meV compared to PCBM because of bis adduct of the methanofullerene derivative, resulting in an increase of $V_{oc}$ in devices with P3HT.

Experimental Section

NMR spectroscopy was conducted using Bruker Avance 300 spectrometer. NMR-solvents were purchased from Deutero. The chemical shifts are reported in part per million (ppm) and referenced to the residual solvent. Spectral splitting patterns are designated as “s” (singlet), “d” (doublet), “m” (multiplet). The raw data was processed using MestReNova Lite.

$^1$H NMR spectra were recorded on Bruker DPX 300 (300 MHz) spectrometer and chemical shifts are reported as δ values (ppm) and referenced to residual $^1$H signals in deuterated solvents.

Absorption profiles were recorded with a Perkin-Elmer Lambda-35 absorption spectrometer from 350 to 1100 nm. UV measurements were performed with an Metrohm Autolab III/FRA2 potentiostat/galvanostat. PL data were collected using a Perkin–Elmer LS55 Fluorescence Spectrometer. Unless otherwise stated, the PL excitation wavelength was set to 488 nm (approximately the absorption maximum for P3HT).

Bulk heterojunction devices were fabricated using polymers as electron donors and PC$_{60}$BM (Solenne) as electron acceptor. The standard device structure was as follows: ITO/PEDOT:PSS (AL4083, H.C. Stark) solution diluted in isopropanol was doctor-bladed onto clean substrates, resulting in a thickness as actual devices were fabricated for space charge limited current (SCLC) measurements. A PEDOT:PSS (AL4083, H.C. Stark) solution diluted in isopropanol was doctor-bladed onto clean substrates, resulting in a thickness of approximately 40 nm as determined with Dektak profilometer. PEDOT:PSS layer was annealed for 15 min at 140 °C in nitrogen filled glovebox. The active layer consisting of P3HT (10 mg/ml) and NCBA was stirred at 65 °C for 12 h before use. The active layers from chlorobenzene (CB) solution with different weight ratios were doctor-bladed onto PEDOT:PSS layer (~100nm). A Ca/Ag (~15/85nm) top electrode was evaporated via a mask in vacuum onto the active layers with an electrode area of 0.104 cm$^2$. PCE was calculated from J-V characteristics recorded with Botest source measure unit by an Oriel Sol1A 94061 solar simulator with an intensity of 100 mW/cm$^2$ where the light intensity was calibrated with a standard silicon photodiode. The EQE spectra were recorded with a Varian Cary 500 Scan spectrometer with tungsten light source using a lock-in amplifier.

The electron and hole only devices with the same active layer thickness as actual devices were fabricated for space charge limited current (SCLC) measurements. A $R_S$ of 0Ω is considered for the voltage correction; $V = V_{app} - V_{bd} - V_{rd}$ where $V$ is the effective voltage, $V_{app}$ is the applied voltage, $V_{bd}$ is the voltage drop and $V_{rd}$ is the built-in voltage. The hole mobility was calculated by fitting dark J-V curves to SCLC model in which the current density is given by $J = 9e_0\varepsilon_r\mu V^2/8L^2$, where $e_0$ and $\varepsilon_r$
represents the permittivity of the material, μ is the mobility and L is the thickness of the active layer.

Morphology of the films were observed by Atomic Force Microscopy using Ambios AFM equipment.

5 Electrochemistry

The electrochemical properties of compound NCBA have been studied at room temperature by means of cyclic voltammetry (CV). The cyclic voltammograms are collected using a CH-Instrument 660 B Model electrochemical analyzer. A three electrode cell set-up employed for the measurements consisted of glassy carbon working electrode, Pt wire counter electrode and Ag/AgCl reference electrode, all placed in a glass vessel. Tetrabutylammonium hexafluorophosphate (TBAPF₆), 0.1 M, was used as supporting electrolyte. Ferrocene was used as internal reference electrode. The electrochemical properties of the NCBA are examined by cyclic voltammetry in o-DCB/MeCN (4:1) solvent mixture with 100 mV/s scan rate. Compound NCBA display the typical redox behaviour of a [60]fullerene derivative, with quasi-reversible reduction waves at -0.49, -0.87 and -1.38 V (Figure 2). Cyclic voltammogram was presented in Figure 2 and all redox potentials of dimers are summarized in Table 1.

Characterization

25 Synthesis of 4-propylpentyl-p-tosylhydrazone (3)

To a solution of 4-nonanone (1) (1g, 7 mmol) and p-toluene sulfonyl hydrazide (2) (1.3 g, 7 mmol) in 25 ml toluene, 0.33 ml acetic acid are added under argon atmosphere. The resulting mixture is stirred for 8 hours at 110 °C. Then, the solvent is evaporated. Crude product is extracted with hexanes containing acid water (5% HCl) solutions, then washed with water for three times, and dried over magnesium sulfate. The product is obtained as a yellow oil (85%).

\[ ^1H-NMR\ (CDCl_3,\ 400\ MHz)\ \delta\ (ppm)\ =\ 7.85\ (2H,\ d),\ 7.29\ (2H,\ d),\ 2.42\ (3H,\ s),\ 2.11\ (4H,\ m),\ 1.2-1.8\ (8H,\ m),\ 0.9\ (6H,\ m). \]

Synthesis of bis-4-propylpentyl[6, 6]methanofullerene (NCBA) (4)

To a solution of 3 (100 mg, 0.32 mmol) in 4 ml of dry pyridine, sodium methoxide (20 mg, 0.38 mmol) is added under argon atmosphere. After stirring at room temperature for 15 minutes, a solution of [60]fullerene (115 mg, 0.16 mmol) in 20 ml of o-DCB is added at once and the mixture is then heated at 180 °C for 18 hours. After cooling to room temperature, the solvent is evaporated. Purification by FC (SiO₂/hexanes) followed by recycle preparative HPLC-GPC/GFC (Agilent Pl-gel 10 µm MIXED-D, and Nucleogel GFC 500-10, 15 mL/min toluene) gave 4 as a brown solid (20%). Synthesis procedure was done according to literature with small modifications.

1H-NMR (CDCl₃, 400 MHz) δ (ppm) = 1.6-1.3 (24H, m), 0.84 (12H, t). Calcd: C 95.78, H 4.22; found C 95.75 H 4.20. Mass (m/z): 972. Mass spectra supplied in Supporting Information (ESI).

Optical and Electrochemical Properties

Figure 1. a) UV-vis absorption spectra of NCBA and PCBM films and b) Photoluminescence quenching of P3HT using 50% NCBA excited at 488 nm.

Absorption in the visible region is a significant property for the acceptor material in organic photovoltaics (OPV)s. In literature, PCBM and indene bis-adduct ICBA are superior to PCBM mainly due to their stronger absorption in the visible region. Figure 1 represents the UV-vis absorption spectra of both PCBM and NCBA in thin film. The absorbance of NCBA is stronger in visible region between 400 nm and 500 nm than that of PCBM.

Table 1. Redox Potentials (CV) of bis-4-propylpentyl[6, 6]methanofullerene. V vs Ag/AgCl; GCE as the working electrode; 0.1 M Bu₄NPF₆; o-DCB/MeCN (4:1); scan rate 100 mV/s.

<table>
<thead>
<tr>
<th>Potential (V)</th>
<th>PCBM</th>
<th>NCBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CV</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>0.02</td>
<td>0.04</td>
<td>0.06</td>
</tr>
<tr>
<td>0.04</td>
<td>0.06</td>
<td>0.08</td>
</tr>
</tbody>
</table>

This journal is © The Royal Society of Chemistry [year]
The electrochemical properties of NCBA were studied by cyclic voltammetry (Figure 2). The lowest unoccupied molecular orbital (LUMO) was calculated from their onset reduction ($E_{\text{onset red}}$) obtained from the cyclic voltammogram. The LUMO energy level of NCBA is 13.59 eV, which is raised by 0.07 eV in comparison to that of PCBM (3.66 eV) in the same measurement system. The higher LUMO energy level of NCBA is desirable for its application in PSCs to get higher $V_{\text{oc}}$. The shift in the LUMO level toward the vacuum level is due to the presence of the fewer unsaturated bonds as compared with fullerene monoadducts.

<table>
<thead>
<tr>
<th></th>
<th>$E_{\text{1 red}}$ (V)</th>
<th>$E_{\text{2 red}}$ (V)</th>
<th>$E_{\text{3 red}}$ (V)</th>
<th>$E_{\text{ferrocene}}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NCBA</td>
<td>-0.50</td>
<td>-0.87</td>
<td>-1.38</td>
<td>0.71</td>
</tr>
<tr>
<td>PCBM</td>
<td>-0.43</td>
<td>-0.82</td>
<td>-1.33</td>
<td>0.71</td>
</tr>
</tbody>
</table>

Photovoltaic properties

Photovoltaic performances of NCBA are investigated with P3HT as donor group in the normal structure BHJ solar cells using different donor: acceptor ratios. In BHJ devices, the weight ratio of donor/acceptor plays a significant role and has a large effect on PCE due to the balance between the absorption and the charge transport network of the active layer. Therefore, different weight ratios (2:1, 1:1, 1:2) for P3HT: NCBA (10mg/ml) were prepared using chlorobenzene (CB) for device fabrication and 50% NCBA loading (1:1) was found to be the optimized ratio. When reporting improvements in photovoltaic performance, it is critical to provide sufficient information in the form of statistics and experimental conditions to enable the work to be reproduced, and to allow the reader to evaluate the reliability of the data. Therefore, the $J-V$ characteristics of P3HT: NCBA devices, under illumination, using different D:A ratios and the effect of annealing to the best ratio are shown in Figure 3 and the key parameters from the average 6 devices are summarized in Figure 4 and Table 2. As seen from Figure 3, low amount of acceptor addition suffers from the low current in 2:1 ratio (3.9 mA/cm$^2$) P3HT: NCBA cells. Thermal annealing the best ratio of P3HT:NCBA (1:1) at 140 °C for 5 min. increased the fill factor remarkably from 53% to 65% and relatively high open circuit voltage ($V_{\text{oc}}$) of 0.73 V was observed which is much higher than that of conventional P3HT:PCBM cells. Higher loading of NCBA to the blend system decreased the short circuit current ($J_{\text{sc}}$) and the open circuit voltage ($V_{\text{oc}}$) which is due to transport properties in the blend. The preliminary performance results of best P3HT: NCBA solar cells are confirmed by external quantum efficiency (EQE) measurement. Figure 5 exhibits the EQE of not annealed and annealed best ratio P3HT: NCBA cells. From EQE measurements, the short-circuit current density (under air mass (AM) 1.5 conditions) was estimated to be 5.9 mA/ cm$^2$ for 1:1 P3HT: NCBA cell suggesting that the photon-electron conversion processes are rather efficient. Figure 6 shows the atomic force microscopy (AFM) images of 1:1 P3HT:NCBA solar cell before annealing (b) and after annealing (c) in noncontact mode. Annealing improved the surface morphology and increased the efficiency of 1:1 ratio P3HT:NCBA solar cell.
Figure 4. Average key parameters of P3HT:NCBA solar cells from 6 devices.

Table 2. Key parameters of P3HT:NCBA solar cells using different D:A ratios and comparison with P3HT:PCBM solar cell.

<table>
<thead>
<tr>
<th>Donor: Acceptor Ratio (w:w)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>0.65</td>
<td>3.9</td>
<td>59.7</td>
<td>1.5</td>
</tr>
<tr>
<td>1:1</td>
<td>0.73</td>
<td>5.9</td>
<td>65.1</td>
<td>2.8</td>
</tr>
<tr>
<td>1:2</td>
<td>0.67</td>
<td>2.6</td>
<td>53.5</td>
<td>0.93</td>
</tr>
<tr>
<td>P3HT:PCBM (1:1)</td>
<td>0.56</td>
<td>6.77</td>
<td>58.7</td>
<td>2.22</td>
</tr>
</tbody>
</table>
This journal is © The Royal Society of Chemistry [year]

Figure 5. External quantum efficiency (EQE) spectra of devices based on P3HT: NCBA with and without annealing.

Figure 6. Atomic Force Microscopy (AFM) Images of NCBA:P3HT (1:1 ratio) based organic solar cells; PEDOT on ITO glass (a); NCBA on PEDOT/ITO surface before annealing (b); NCBA on PEDOT/ITO surface after annealing (c).

Layers of NCBA and P3HT: NCBA were investigated to determine the charge transport properties. Charge carrier mobilities in NCBA and in the blend were measured by the space charge limited current (SCLC) method. The SCLC mobility measures the hole and electron mobility in the direction perpendicular to the electrodes; thus, it is the most representative measurement of charge-carrier mobility for solar cells. To measure the hole and electron mobilities of different fullerene derivative blends, the ITO/PEDOT:PSS/active layer (100nm)/PEDOT:PSS/Ag (100nm) and ITO/AZO/active layer/Ca (15nm)/Ag (85nm) devices were fabricated, respectively. Table 3 summarizes electron and hole mobilities for NCBA and P3HT: NCBA blends with and without thermal annealing (See Figure S1-3). Electron mobility of NCBA was found to be comparable to PCBM and was decreased one order of magnitude in the annealed blend. The parameter that represents the ratio of the hole-to-electron mobilities ($\mu_h/\mu_e$) in the D:A blends is crucial to understand the optoelectronic properties of BHJ, particularly with respect to FF. It is known that balanced charge-carrier transport is an important factor for increasing the fill factor (FF) in BHJ solar cells. Annealed 1:1 ratio P3HT:NCBA films showed a relatively balanced $\mu_h/\mu_e$ value in the same order yield in high FF in the devices.

Table 3. Summary of electron and hole mobilities ($\mu_e$ and $\mu_h$) of pristine NCBA and blends with P3HT. The values were obtained from the J-V curves (see SI) and Mott-Gurney equation and represent an average mobility over the thickness range measured.

<table>
<thead>
<tr>
<th></th>
<th>Hole mobility (cm²/Vs)</th>
<th>Electron mobility (cm²/Vs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine NCBA</td>
<td>9.4x10⁻⁵</td>
<td>2.14x10⁻³</td>
</tr>
<tr>
<td>P3HT:NCBA 1:1 not annealed</td>
<td>1.04x10⁻⁴</td>
<td>1.24x10⁻⁵</td>
</tr>
<tr>
<td>P3HT:NCBA 1:1 annealed</td>
<td>8.84x10⁻⁴</td>
<td>1.14x10⁻⁴</td>
</tr>
</tbody>
</table>

CONCLUSION

In summary, we have successfully synthesized a bis-adduct C₆₀ derivative using a nonyl solubilizing group with simple synthetic route. NCBA offers a higher LUMO level compared to that of PCBM in order to minimize the energy losses in the electron transfer from the donor to the acceptor material. Besides a high electron mobility of 2x10⁻³ cm²/Vs, NCBA showed slightly higher absorption in 400-500 nm region compared to PCBM. Bulk-heterojunction photovoltaic devices are constructed using the fullerene derivative as acceptor with P3HT donor and efficiencies up to 2.8% have been achieved without further device optimization. As depicted, higher LUMO level resulted in significantly enhanced $V_{oc}$ of 0.73V. Our successful preliminary results suggested that further optimization of this novel fullerene bis-adduct can yield higher efficiencies with chemical modifications to fine tune the electronic properties and different conjugated polymers can be used to achieve higher power conversion efficiencies.
Acknowledgement
The authors gratefully acknowledge the Cluster of Excellence “Engineering of Advanced Materials” at the University of Erlangen-Nuremberg, which is funded by the German Research Foundation (DFG) within the framework of “Excellence Initiative”. S. Ella acknowledges Alexander von Humboldt Foundation (AvH), Turkish Scientific and Technological Research Council (TUBITAK), UNESCO-LOREAL Foundation and Turkish Academic of Sciences (TUBA). D. Baran acknowledges Bavarian Research Foundation and the project Synthetic Carbon Allotropes (SFB953).

Notes and references


29) Zhao, G.; He, Y.; Li, Y. 6.5% Efficiency of Polymer Solar Cells Based on poly(3-hexylthiophene) and Indene-C60 Bisadduct by Device Optimization. *Adv. Mater.* 2010, 22, 4355-4358.


