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ARTICLE TYPE

Facile Synthesis and Photovoltaic Applications of a New Alkylated Bismethano Fullerene as Electron Acceptor for High Open Circuit Voltage Solar Cells

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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 C_{60} are of high interest for improving the V_{oc} in BHJ solar cells. In this work, we have developed a novel bis-4-propylpentyl [6,6] methanofullerene bis-adduct, NCBA, using a 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 V_{oc} of 0.73 V.

Introduction

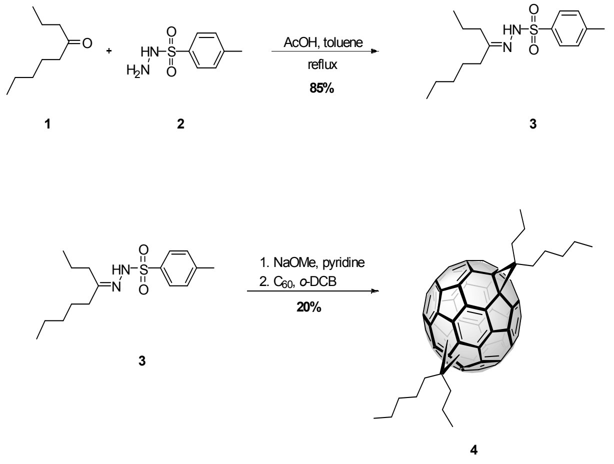
The power conversion efficiencies of organic photovoltaic devices have been swiftly increased in the last years to 11% for single junction polymer: fullerene cells.[1-3] Poly(3-hexylthiophene) (P3HT) is the widely used commercial conjugated polymer donor material, and [6,6]-phenyl-C-61- butyric acid methyl ester (PCBM) is the most important soluble C_{60} 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.[4,5] 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.[6] 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.[6-12] Nevertheless, the research efforts toward new C_{60} derivative acceptor materials to replace PCBM have not been very successful until now with different polymer donors.[13-15]

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 (V_{oc}) in PSCs, since V_{oc} is strongly related to the difference between the LUMO level of acceptor and the HOMO of the donor material.[16-18] 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 C_{60} derivatives and a new C_{84} derivative have been synthesized and utilized as acceptors in OPVs, only handful C_{60} 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.[19-20] 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.[21-28]

Among these electron acceptors based on fullerene, fullerene bisadducts, which have two solubilizing groups, effectively increase V_{oc} 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.[29]

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 0.15 V higher than that of P3HT:PCBM due to the higher LUMO energy level of bis-PCBM as compared to PCBM.[30] Afterwards, Laird and Li et al.[26,29,31] reported a remarkable bis-adduct fullerene derivative, indene-C_{60} bis-adduct (ICBA). Through the Diels-Alder reaction of indene with the 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 *o*-dichlorobenzene (*o*-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.



Scheme 1. Synthetic route to bis-4-propylpentyl [6,6] methanofullerene NCBA.

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 date was processed using MestReNova Lite.

Mass spectrometry (MS) was done on a Shimadzu AXIMA Confidence MALDI-TOF MS-spectrometer (nitrogen UV-laser, 50 Hz, 337 nm). ESI mass spectrometry was carried out on a Bruker maxis 4G UHR TOF MS/MS-Spectrometer.

^{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. CV measurements were performed with an Metrohm μ 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 $PC_{61}BM$ (Solenne) as electron acceptor. The standard device structure was as follows: ITO/PEDOT:PSS (AL4083)/ Polymer:$PC_{61}BM$/Ca/Ag. ITO coated glass was used as transparent electrode. ITO was cleaned by ultrasonic treatment with acetone and isopropyl alcohol and dried under a flow of dry nitrogen. 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 a 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 chage limited current (SCLC) measurements. A R_s of 4Ω is considered for the voltage correction; $V= V_{appl}-V_{bi}-V_{rs}$, where V is the effective voltage, V_{appl} is the applied voltage, V_{rs} is the voltage drop and V_{bi} 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 $J = 9\varepsilon_0\varepsilon_r\mu V^2/8L^3$, where ε_0 and ε_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.

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. Tetrabutylamonium hexafluorophosphate (TBAPF$_6$), 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 voltammagram was presented in Figure 2 and all redox potentials of dimers are summarized in Table 1.

Characterization

*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 acidic 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%).

^{1}H-NMR (CDCl$_3$, 400 MHz) δ (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 (SiO$_2$/hexanes) followed by recycle preparative HPLC-GPC/GFC (Agilent PLgel 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.[32]

^{1}H-NMR (CDCl$_3$, 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

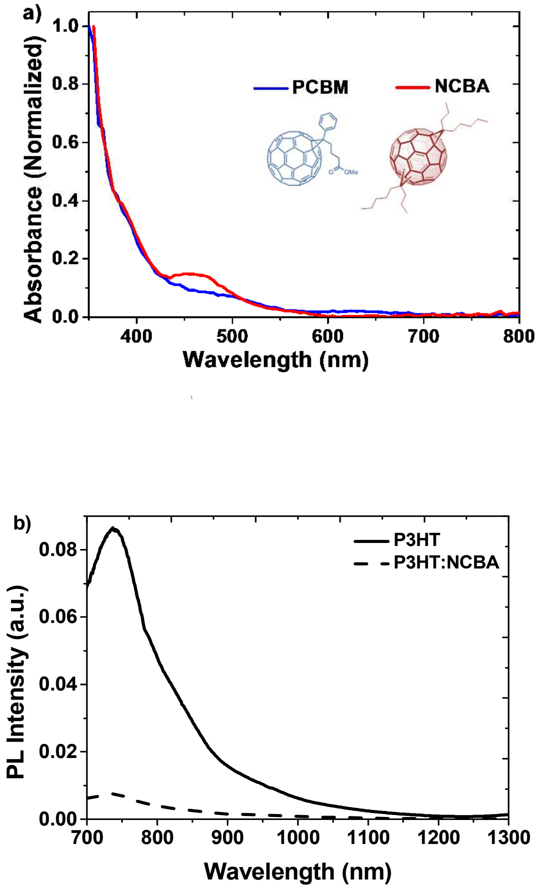


Figure 1. a) UV-vis absorption spectra of NCBA and PCBM films and b) Photoluminescence quenching of P3HT using 50% NCBA excited at 488 nm.

Absorption in the visible region is a significant property for the acceptor material in organic photovoltaics (OPV)s. In literature, PC$_{70}$BM and indene bis-adduct ICBA are superior to PCBM mainly due to their stronger absorption in the visible region.[21] 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 Bu$_4$NPF$_6$; *o*-DCB/MeCN (4:1); scan rate 100 mV/s.

	E^{1}_{red} (V)	E^{2}_{red} (V)	E^{3}_{red} (V)	$E_{ferrocene}$ (V)
NCBA	-0.50	-0.87	-1.38	0.71
PCBM	-0.43	-0.82	-1.33	0.71

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^{onset}_{red}) obtained from the cyclic voltammogram. The LUMO energy level of NCBA is -3.59 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_{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.

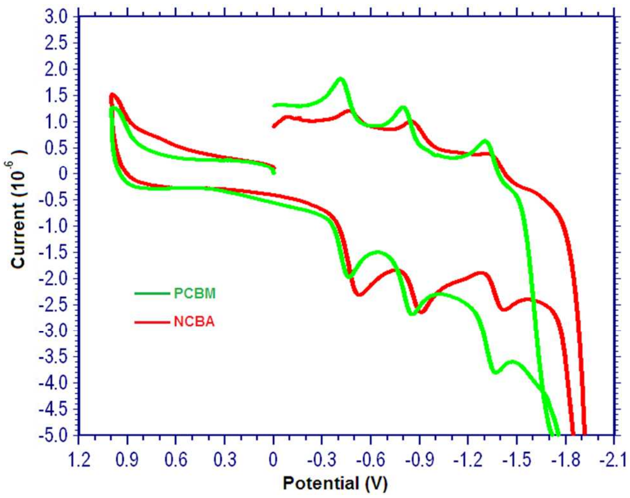


Figure 2. Cyclic voltammogram of NCBA (under N_2, 0.1 M Bu_4NPF_6 in *o*-DCB/MeCN (4:1) solution mixture, vs Ag/AgCl; GCE as the working electrode, scan rate 0.1 V/s. internal standard Fc/Fc^+ $E_{1/2}$ at 0.68 V)

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.[33] Therefore, different weight ratios (2:1, 1:1, 1:2) for P3HT: NCBA (10mg/ml) were prepared using cholorobenzene (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.[34-36] 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_{oc}) of 0.73 V was observed which is much higher than that of conventional P3HT:PCBM cells.[37] Higher loading of NCBA to the blend system decreased the short circuit current (J_{sc}) and the open circuit voltage (V_{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.

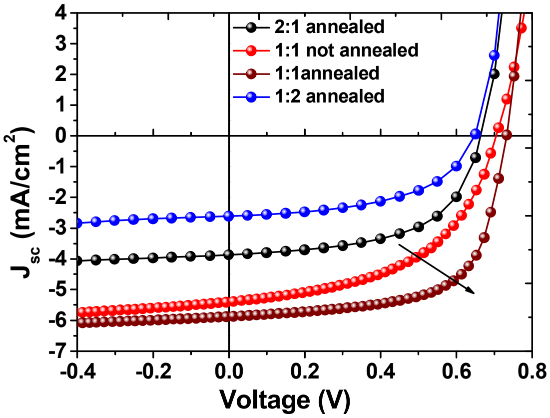
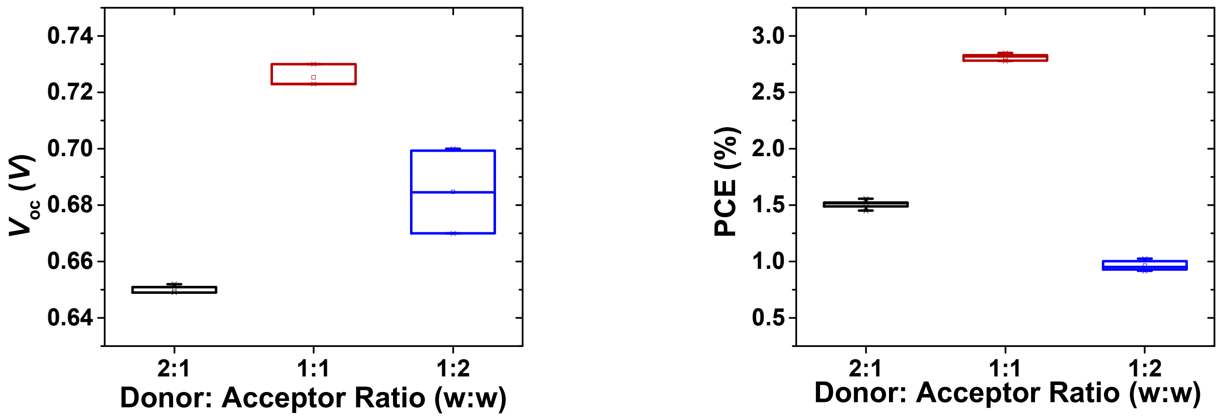
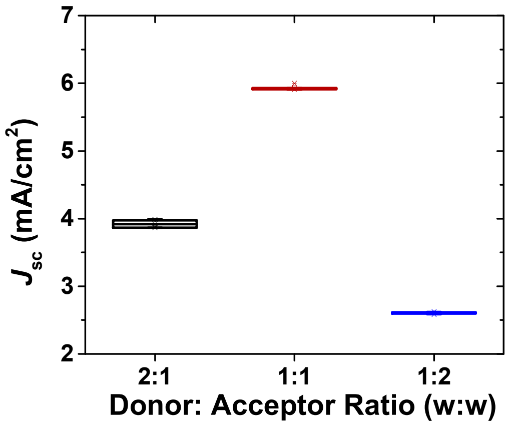


Figure 3. *J-V* characteristics of P3HT: NCBA devices using different donor: acceptor ratios, under illumination at 100mW/cm^2.





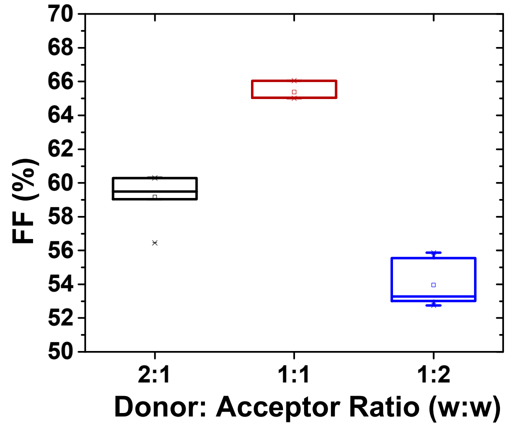


Figure 4. Average key parameters of P3HT:NCBA solar cells from 6 devices

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

P3HT:NCBA annealed	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	PCE (%)
2:1	0.65	3.9	59.7	1.5
1:1	0.73	5.9	65.1	2.8
1:2	0.67	2.6	53.5	0.93
P3HT:PCBM (1:1)	0.56	6.77	58.7	2.22

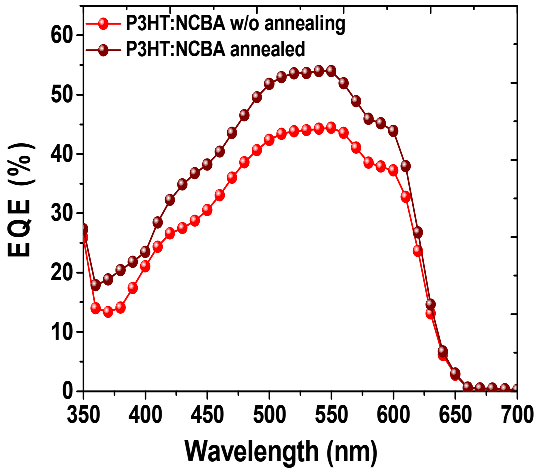


Figure 5. External quantum efficiency (EQE) spectra of devices based on P3HT: NCBA with and without annealing.

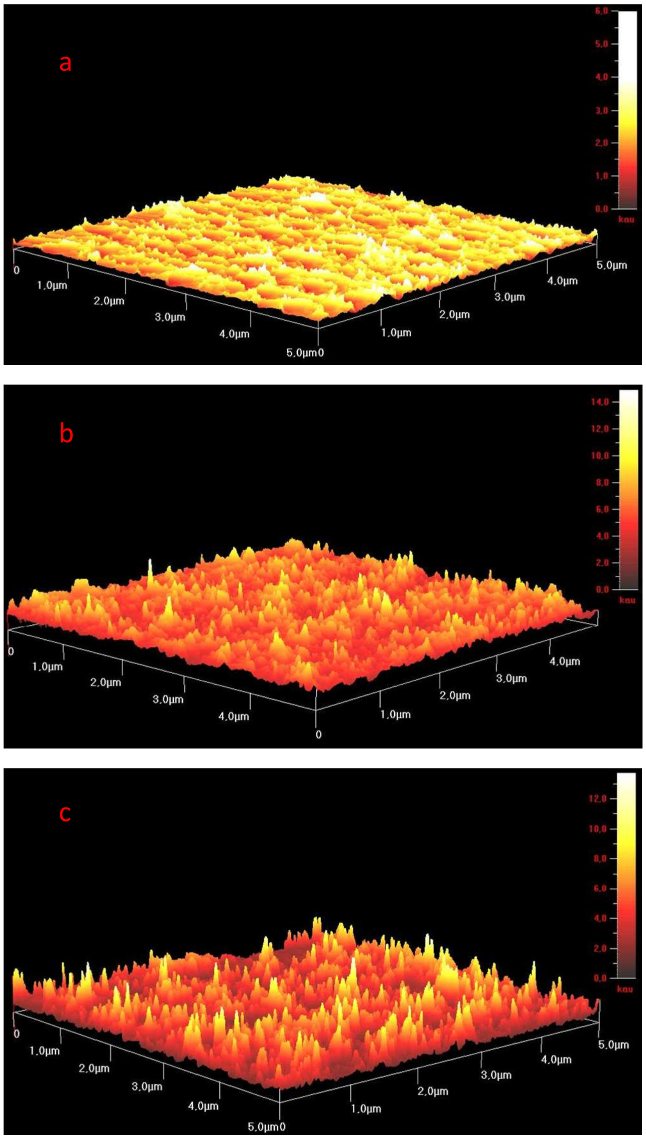


Figure 6. Atomic Force Microscopy (AFM) Images of NCBA:P3HT (1:1 ratio) based organic solar cells; PEDOT on ITO glass (a); NCBA on PEDOT/ITO surface before annealing (b); NCBA on PEDOT/ITO surface after annealing (c).

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.[38-39] 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 SI-3*). Electron mobility of NCBA was found to be comparable to PCBM[40] and was decreased one order of magnitude in the annealed blend. The parameter that represents the ratio of the hole-to-electron mobilities (μ_h/μ_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 μ_h/μ_e value in the same order yield in high FF in the devices.

Table 3. Summary of electron and hole mobilities (μ_e and μ_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.

	Hole mobility (cm^2/Vs)	**Electron mobility (cm^2/Vs)**
Pristine NCBA	$9.4x10^{-5}$	$2.14x10^{-3}$
P3HT:NCBA 1:1 not annealed	$1.04x10^{-4}$	$1.24x10^{-5}$
P3HT:NCBA 1:1 annealed	$8.84x10^{-4}$	$1.14x10^{-4}$

CONCLUSION

In summary, we have successfully synthesized a bis-addcut C_{60} 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 $2x10^{-3}$ cm^2/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.

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