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European Chemical Societies Publishing

Accepted Article

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.202000354

Link to VoR: https://doi.org/10.1002/cplu.202000354

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A Cross-Linkable Electron Transport Layer Based on a Fullerene– Benzoxazine Derivative for Inverted Polymer Solar Cells

Sandeepa Kulala Vittala,^[a] Remya Ravi,^[a] Biswapriya Deb*^[a] and Joshy Joseph*^[a]

Abstract: Herein, the synthesis, optoelectronic characterization and device properties of a new cross-linkable fullerene derivative, [6,6]phenyl- C_{61} -butyric benzoxazine ester (**PCBB**) is reported. The PCBB inherits all the basic photophysical and electrochemical properties of parental [6,6]-phenyl-C₆₁-butyric methyl ester (**PCBM**). Thermal cross-linking of the benzoxazine moiety in PCBB resulted in the formation of cross-linked, solvent resistive adhesive films (C-PCBB). Atomic force microscopy (AFM) and optical microscopic studies showed dramatic reduction in the roughness and aggregation behaviour of P3HT-PCBM polymer blend film upon incorporation of C-PCBB interlayer. An inverted bulk hetero junction solar cell based on the configuration ITO/ZnO/C-PCBB/P3HT-PCBM/V₂O₅/Ag achieved 4.27% power conversion efficiency (PCE) compared to the reference device ITO/ZnO/P3HT- PCBM/V2O5/Ag (PCE=3.28%). This 25% increment in the efficiency is due to the positive effects of C-PCBB on P3HT/C-PCBB and PCBM/C-PCBB heterojunctions.

Introduction

In the recent decades, polymer solar cells (PSCs) received widespread interest in the scientific community due to their potential application in fabrication of light weight and flexible electronics by low-cost solution processing techniques.^[1] In order to increase the donor-acceptor interfacial area in the polymer blend for efficient exciton dissociation and charge transport, the concept of bulk heterojunction (BHJ) composing bicontinuous interpenetrating nanonetwork of polymer blend containing p-type donor and n-type acceptor architecture have been adopted.^[2] The poly(3-hexylthiophene) (P3HT) and [6,6]phenyl-C₆₁-butyric acid methyl ester (PCBM) donor-acceptor combination was used as a standard to understand the role of active layer morphology towards efficient BHJ-Polymer Solar Cell (BHJ-PSC) device which reached power conversion efficiency (PCE) >5% and is being used as a reference system till today.^[3] Previously, many groups have shown improved efficiency by introducing innovative polymer donors, [3b] fullerene acceptors^[4] and incorporating new interfacial electron/hole transport layers.^[5] Also, the inverted PSC configuration is most suited to realize stable and long lasting device than conventional architecture.^[6] Modified fullerene derivative such as indene C60bisadduct.^[7] fullerene-di(4-methyl-phenyl)methano-C₆₀ (DMPCBA),^[8] bis-o-quino-dimethane C₆₀ (Bis-QDMC)^[9] etc. in

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the presence of **P3HT** donor shown improved PCE compared to reference **PCBM** acceptor.

On the other hand, it has been demonstrated that the nanoscale morphology of BHJ active layer tend to undergo macrophase separation due to the high aggregation/crystallization tendency of fullerene molecules.[2a] When solar cells are working under natural conditions, such an aggregation will enhance with time due to continuous heat-cool cycles, which will hamper the device performance.^[10] Therefore, to create stable and high life time PSCs for practical applications, stable BHJ film morphology is highly essential.^[11] One of the strategies is to "freeze" the active layer nano-structure obtained after spin coating.^[12] In this line, cross-linking approach have been developed using cross-linkable groups such as epoxide,^[13] halide,^[14] azide,^[15] oxetane,^[16] and styrene.^[17] These moieties were successfully substituted into the side chains of the polymer or fullerene and have shown promising results in terms of stable nanostructures and devices.[18] Also, many cross-linking reactions namely, click reaction,[19] disulfide bond formation,[19a] olefin metathesis,^[19a, 20] have been introduced to retain the supramolecular nanostructure. For example, Yongfang Li et al. reported that the P3HT-ICBA based inverted device with C-PCBSD electron extracting interlayer improves the PCE to a remarkable 6.2% through electronic and orbital interactions at the interface.^[21] Later the same group fabricated vertically aligned C-PCBSD fullerene derivative as ETL instead of crosslinked film using the same P3HT-ICBA polymer blend system and achieved record high PCE of 7.4% due to the high charge transport across the vertical nanorods of ETL.[22] Using similar strategy many cross-linkable fullerenes has been used as ETL in BHJ-PSCs^[11a, 16, 23] and perovskite solar cells.^[24] These highest efficiencies achieved using modified fullerene derivatives in the presence of P3HT electron donor shows the requirement and role of fullerene functionalization towards simple and stable PSC device with improved efficiencies.

The functionalization of cross linkable fullerenes can be achieved, either covalently attaching cross-linkable units to fullerene monomer or by external addition of reactive species during solution processing which could undergo cross-linking upon thermal annealing^[18] or oxidative polymerisation.^[25] The first method maintains the organization of fullerenes along the polymerizable groups facilitating a possible stable nanostructure via self-assembly through non-covalent interactions.^[26] On the other hand, the second approach sometimes fails in controlling desired nano-morphology.^[27] Recently, cross-likable the benzoxazine derivatives gather tremendous attention due to their excellent properties including, low water absorption, nearzero volumic shrinkage upon curing and low coefficient of thermal expansion,.^[28] Moreover, they can be easily synthesized from conventional cheap precursors and crosslinked under heat triggered reaction, without the aid of external initiators or catalysts.^[29] In the present work, we have undertaken covalent functionalization of fullerene with benzoxazine cross-linkable group, explored the morphological

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Scheme 1. Synthetic scheme for cross-linkable fullerene derivative, **PCBB** under study. EDC: 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide, DMAP: 4-(dimethylamino)-pyridine, ODCB: *ortho*-dichlorobenzene.

and optoelectronic properties and demonstrated their potential application as ETL in BHJ-PSCs.

Results and Discussion

Synthesis and Characterization of PCBB

The synthesis of [6,6]-Phenyl-C₆₁-butyricbenzoxazine ester, **PCBB** with benzoxazine cross-linkable group was carried out as shown in Scheme 1. The starting materials [6,6]-phenyl C₆₁butyric acid (PCBA), obtained by the ester hydrolysis of **PCBM** and methylol benzoxazine (MB) were synthesized following reported literature procedures.^[28a, 29] Subsequently, the final **PCBB** derivative was synthesized via EDC-DMAP coupling of PCBA and MB in *ortho*-dichlorobenzene (ODCB) to obtain the desired final product **PCBB**. The structural characterization of **PCBB** was accomplished through FT-IR, ¹H NMR, ¹³C NMR, UV-visible and MALDI-TOF mass spectral analysis.

Photophysical Properties of PCBB

Since, the core structure of **PCBB** resembles its parental derivative **PCBM**, we have studied the photophysical properties of **PCBB** in comparison to **PCBM** using UV-Visible absorption spectroscopy, square wave voltammetry (SWV), thermogravimetric analysis and **P3HT** fluorescence quenching experiments. Typical UV-Visible absorption spectra of **PCBB** in chloroform showed the characteristic peak at 328 nm, which is similar to that of **PCBM** (Figure 1a).^[30]

The electrochemical properties of **PCBB** and **PCBM** were compared by using SWV method. SWV is pulse voltammetry technique which is carried out by monitoring the current using staircase-shaped voltage ramp over a range of set values. The current measured at the end of forward/reverse pulse provides information in the form of a peak for each oxidation/reduction processes. This method is advantageous over conventional voltammetry due to its fast analysis and high sensitivity with a wide dynamic range of electroactive materials. Moreover, in SWV deoxygenation of the solution is not required unless it interferes with the electrode reaction. The disadvantage of SWV is the lack of information regarding the reversibility of redox species. Measurements were carried out using the thin films of fullerene derivatives on glassy carbon electrode with Ag/AgCI as a reference electrode, calibrated by ferrocene ($E_{1/2(ferrocene)} = 0.45$ V vs. Ag/AgCI). Both compounds exhibited identical first reduction potential of -0.57 V vs Ag/Ag⁺ (Figure 1b). The LUMO energy levels were calculated relative to the reference energy level of ferrocene (4.8 eV below the vacuum level) using the equation (1).^[31]

 $E_{HOMO/LUMO} = - [4.8 + E_{ox/red} - 0.45] eV \dots (1)$ The HOMO/LUMO energy levels of both compounds were found to be -5.5 eV and -3.78 eV, respectively indicating negligible perturbation in electronic properties upon substitution. The reduction potentials and LUMO energy levels of fullerene derivatives were summarized in Table S1. Further, DFT calculations of the neutral **PCBB** and **PCBM** were performed at the B3LYP/6-31G (d, p) level and optimized their HOMO and LUMO energies in vacuum conditions. The geometry optimization provided HOMO and LUMO energy levels of -5.65 eV and -3.09 eV for both **PCBB** and **PCBM** (Figure S1). The comparable HOMO/LUMO energy values of **PCBB** and **PCBM** indicate that benzoxazine substitution does not perturb the electronic properties of the **PCBB** derivative.

We have investigated fluorescence quenching of **P3HT** donor in the presence of **PCBB** and **PCBM** fullerene derivatives to assess the electron transport properties. The fluorescence intensity of **P3HT** at 585 nm (λ_{max}) decreased with increasing concentration of both **PCBB** and **PCBM** (Figure S2a and S2b). This is mainly attributed to the intermolecular electron transfer from **P3HT** donor to the fullerene acceptor due to their



Figure 1. (a) Normalized absorption spectra of PCBB and PCBM in chloroform. (b) Square wave voltamogram of PCBB and PCBM vs Ag/AgCl at a scan rate of 100 mV s⁻¹. (c) Stern-Volmer plot of PCBB and PCBM obtained from P3HT fluorescence quenching studies. (d) TGA profiles of PCBB and PCBM; the black lines in thermogram indicate the T_d value.

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favorable HOMO-LUMO energy levels.^[32] In order to understand the quenching efficiency of **PCBB** fullerene derivative compared to parental **PCBM** the Stern-Volmer constant was calculated using the equation

where F_o and F are the fluorescence intensities in the absence and presence of the quencher, respectively, Ksv is the Stern-Volmer quenching constant, and [Q] is the concentration of the quencher. The Stern-Volmer plots revealed linear increment for both **P3HT-PCBM** and **P3HT-PCBB** which is characteristic of dynamic quenching (Figure 1c). The Ksv for **P3HT-PCBM** and **P3HT-PCBB** was calculated to be 5.63 x 10³ M⁻¹ and 4.35 x 10³ M⁻¹, respectively. The Ksv value for **P3HT-PCBM** is quite similar to that reported in the literature.^[33] Ksv, is indicative of the quenching interactions within the donoracceptor system and **PCBB** derivative has slightly lower value compared to **PCBM** due to the presence of bulkier benzoxazine cross-linking group. Therefore, we have used **PCBB** as crosslinkable electron-transport layer along with **P3HT-PCBM** donoracceptor systems.

Further, the thermal stability of **PCBB** was measured and compared with **PCBM** through thermogravimetric analysis (TGA) before carrying out thermal cross-linking experiments. The TGA profile of both **PCBB** and **PCBM** showed thermal stability up to a temperature of 400 °C and exhibited 5% weight loss (T_d) at 416 °C and 488 °C, respectively (Figure 1d). The relative lower T_d value of **PCBB** is attributed to the bulkier benzoxazine moiety at the ester linkage compare to methyl group in **PCBM**. The



Figure 2. (a) DSC thermogram of **PCBB** at a heating rate of 10 °C min⁻¹. (b) Solid state FT-IR spectra of the **PCBB** and **C-PCBB**. (c) Chemical structures of **PCBB** and **C-PCBB** indicating the functional group transformation upon thermally triggered cross-linking.

thermal characterization studies indicate that the benzoxazine derivative, **PCBB** is thermally stable under the experimental conditions and can be used for thermal curing studies.

Cross-linking and Solvent Resistive Properties

The thermal transition properties of **PCBB** monomer were investigated through Differential Scanning Calorimetry (DSC)



Figure 3. Absorption coefficient of the (a) **C-PCBB** film before (red) and after (blue) rinsing with chloroform and non-cross-linked **PCBB** layer after rinsing with chloroform (black); (b) **PCBM** film before rinsing (red) and after heating followed by rinsing with chloroform (blue). (c) Photograph of glass coated **PCBB** film (thickness *ca.* 135 nm) dipped in chloroform, before and after cross-linking at 200 °C for 15 min.

analysis (Figure 2a). It exhibited a broad exothermic peak with a T_{max} value around 210 °C, indicating the thermal cross-linking of benzoxazine groups.^[28b] The functional group transformation before and after heat cross-linking at 200 °C for 15 min were monitored using FT-IR spectroscopy (Figure 2b). The FT-IR spectrum of **PCBB** after heating showed disappearance of peak at 948 cm⁻¹, characteristic to the out of plane bending vibrational mode of benzene -C-H to which oxazine ring was attached.[34] Moreover, heat cross-linking results in the appearance of a new peak at 3315 cm⁻¹, which is attributed to the phenolic -OH stretching frequency. This confirms thermal cross-linking of PCBB molecule. Based on the reported mechanism of benzoxazine cross-linking in the literature, we propose the heattriggered ring opening polymerisation of benzoxazine group in PCBB, as shown schematically in Figure 2c.^[28a] From these photophysical and cross-linking experiments, we can consider PCBB as a cross-linkable PCBM derivative with similar optoelectronic properties.

To get further insight into the cross-linking behaviour, solid state absorption spectra of PCBB film cured at 200 °C for 15 min on a glass plate was measured before and after rinsing with chloroform (Figure 3a). For comparison, we also used PCBM coated film processed under similar conditions (Figure 3b). Profilometer measurement for the PCBB and PCBM films showed film thickness of 137 nm and 134 nm, respectively (Figure S3). The cross-linked PCBB (C-PCBB) film showed similar absorption properties before and after rinsing, whereas PCBM film completely washed away upon rinsing irrespective of temperature and heating time. As expected, the absorbance of non-cross-linked PCBB film also completely disappeared after rinsing with solvent indicating the importance of curing, without which the material can get washed out by the solvent. This confirms that PCBB forms adhesive films exhibiting excellent solvent resistive property after heat cross-linking. The

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photograph in Figure 3c represents the glass plate with **C-PCBB** and **PCBB** films immersed in beaker containing chloroform which indicates the insoluble nature of **C-PCBB** film and dissolution of non-cross-linked **PCBB** film. These results ascertain that when the temperature is about 200 °C benzoxazine groups of **PCBB** molecule provide adequate flexibility to react in solid state and forms insoluble cross-linked films as proposed in Figure 2c.

Roughness and Crystallization Control

To investigate the applicability of C-PCBB as ETL in BHJ-PSC, the inverted configuration of ITO/ZnO/C-PCBB/P3HT-PCBM/V₂O₅/Ag was adopted. The propensity of C-PCBB layer on the morphology of polymer blend was studied before carrying out device fabrication. Initially ZnO nanoparticle solution prepared using sol-gel process was coated on ITO. The surface of ITO/ZnO showed root mean square (RMS) roughness of 4.68 nm (Figure 4a). Upon coating of C-PCBB laver, the ITO/ZnO/C-PCBB surface exhibited relatively less roughness of 0.31 nm (Figure 4b). The polymer blend was coated without and with C-PCBB laver on ITO/ZnO(Figure 4c and 4d). The surface of polymer blend resulted 2.58 nm roughness with C-PCBB layer and 3.06 nm without C-PCBB. The decreased roughness in the presence of C-PCBB is due to the reduction in the voids of unevenly distributed ZnO by PCBB rendering smoother and more hydrophobic surface. With the view to study solid state properties, the solid state absorption



Figure 4. AFM tapping mode height images of (a) the bare ZnO surface and (b) **C-PCBB** thin film on top of the ZnO. **P3HT-PCBM** polymer blend films (c) without and (d) with **C-PCBB** interlayer after thermal annealing at 120 °C for 10 min, (1.0 ×1.0 μ m). The root mean square roughness was indicated in the insets.

and emission spectra of **P3HT**, **P3HT-PCBM** and **C-PCBB/P3HT-PCBM** were investigated. In the presence of **PCBM**, the absorption spectrum of **P3HT** was unchanged in the region of 400-600 nm while there was an increase in the intensity from 300-400 nm (Figure 5a). Since the film thickness

is same, in case of P3HT-PCBM film there is a decrease in the amount of P3HT with equimolar increase in PCBM. These opposing trends of decreased P3HT absorption and increased PCBM absorption result in net similar absorption compare to P3HT film. But in case of C-PCBB/P3HT-PCBM, there is an additional C-PCBB interfacial layer along with P3HT-PCBM which exhibits increased absorption due to the added absorption from C-PCBB. Also, the shoulder band at 603 nm in the absorption spectrum of the blend indicates the crystallinity of P3HT which remained intact even after blending with PCBM and in the presence of C-PCBB layer. Moreover, the emission maximum of P3HT at 715 nm was quenched to 67% in the presence of PCBM (Figure 5b). For polymer blend with C-PCBB also same amount of quenching was observed. This experiment revealed that incorporation of C-PCBB interlayer increases the absorption of the polymer blend in the visible region without compromising crystallinity of the P3HT polymer.

Another issue with the P3HT-PCBM polymer blend film is their tendency to undergo macrophase separation as a result of crystallization/aggregation of PCBM over the time. The direct contact with the hydrophilic ZnO laver and interfacial erosion is the primary concern. Therefore, the aggregate growth of P3HT-PCBM polymer blend with and without C-PCBB layer was studied using optical microscope. For these studies, the samples of P3HT, P3HT-PCBM and C-PCBB/P3HT-PCBM were analyzed before (10 min annealing) and after ageing for 48 h. It was guite clear that as-prepared films of all three samples were smooth, without exhibiting any kind of aggregation (Figure 5c-e). However, both P3HT and P3HT-PCBM films after 48 hours of ageing showed aggregated crystal like structure indicating macroscopic phase separation of nanomorphology (Figure 5f and 5g). On the other hand, P3HT-PCBM in the presence of C-PCBB interlayer exhibited smooth and homogeneous film under the similar experimental conditions (Figure 5h). This is mainly because of the C-PCBB layer, providing smooth hydrophobic contact to the polymer blend which otherwise in contact with the hydrophilic ZnO, tends to undergo faster crystallization. This further indicates the indirect effect of in situ cross-linking PCBB on the morphological stabilization of polymer blend and inhibition of time dependent macrophase separation.

Photovoltaic properties

BHJ-PSC devices were fabricated with inverted configuration without and with C-PCBB layer to understand the propensity of C-PCBB as ETL. Devices A and B were prepared by spin-coating a mixture of P3HT-PCBM (1:1, w/w) from ODCB to form a ~130 nm thin film on ZnO coated ITO substrates without and with C-PCBB interlayer, respectively. Figure 6 and Table 1 represent the J-V characteristics and summary of photovoltaic performance of the devices A and B, respectively. Under identical fabrication condition reference device A showed a PCE of 3.28% which is in agreement with average reported values for P3HT-PCBM systems.[21a] In the presence of C-PCBB ETL, the PCE of device B was substantially improved to 4.27%. This value signifies a ~25% improvement over device A and is mainly because of simultaneously enhanced open circuit voltage (Voc), short-circuit

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Figure 5. Solid state (a) absorption and (b) emission spectrum of (i) **P3HT** alone (24 mg/mL), (ii) **P3HT-PCBM** blend (1:1, w/w) and (iii) **C-PCBB/P3HT-PCBM**, $\lambda_{exc} = 600$ nm. Optical microscope images of thin films formed from i, ii and iii (c-e) after annealing for 10 min and (f-h) ageing for 48 h (thickness ca. 135 nm).

current (J_{sc}), and fill factor (FF) relative to device A. Both **P3HT** donor and **PCBM** acceptor domains at the interface of BHJ active layer undergo contact with the ZnO bottom layer to form two types of localized nanoscale heterojunctions (Figure 7). Hence, device A contains **P3HT**/ZnO and **PCBM**/ZnO localized heterojunctions at the interface, whereas device B has **P3HT/C-PCBB** and **PCBM/C-PCBB** contact.

Careful analysis of the P3HT domain in the interface we can have following advantages in the case of device B by employing extra C-PCBB layer. In device B, the C-PCBB provides an extra P3HT/C-PCBB interface for exciton dissociation that is more efficient than the P3HT/ZnO interface in device A. Also, the LUMO of C-PCBB (3.8 eV) is situated between the conduction band of ZnO (4.4 eV) and the LUMO of P3HT (3.3 eV). Therefore, the C-PCBB can act as an intermediate energy gradient where electrons can be easily transported to the ZnO layer through cascade pathway. Additionally, we found that the series resistance (R_s) of the device B has a lower value (94.8 Ω cm²) compare to the device A (160.1 Ω cm²). This clearly indicate that the ohmic contact in device B lowers the contact resistance due to the enhanced electrical coupling of PCBB, facilitating better electron transport through the interface. As a result, there might be an efficient electron extraction from the PCBM domain by the C-PCBB interfacial laver. This is in line with the decreased roughness of P3HT-PCBM polymer blend in the presence C-PCBB due to the formation of smooth bicontinuous network (Figure 4c and 4d). These advantages might be associated with the improvement of J_{sc}, from 11.68 mA/cm² (device A) to 12.75 mA/cm² (device B).

Further, the energy difference between the conduction band of ZnO and the HOMO of P3HT (5.2 eV) is only 0.8 eV,

which may give rise to easy charge recombination at the P3HT/ZnO interface in device A. The n-type C-PCBB acting as a hole-blocking layer in device B with energy offset of 1.4 eV relative to 0.8 eV at P3HT/ZnO is still useful for reducing its probability. Moreover, the device B showed higher Voc (0.64 V) relative to the reference device A (0.56 V). This indicate the introduction of C-PCBB in device B act as a hole-blocking layer which prevents the leaky paths by suppressing the back electron transfer from ZnO to P3HT in the active layer. This was reflected by the higher shunt resistance (R_{sh}) of device B (2068.4 Ω cm2) than device A (1177.7 Ωcm2). Hence, in device B the electron transport can occur very efficiently in both heterojunctions of P3HT/C-PCBB and PCBM/C-PCBB while in device A it can happen only at PCBM/ZnO heterojunction. The overall 25% increase in the PCE of the reference device using C-PCBB interlayer confirms that the PCBB act as an efficient crosslinkable electron transport layer in inverted PSCs with efficient exciton separation, decreased charge recombination and interface contact resistance compare to the reference device. The stability of the unencapsulated inverted solar cell devices A and B were periodically monitored by measuring PCEs for



Figure 6. J-V curves of devices A and B under AM 1.5 G illumination at 100 $\,m\text{V/cm}^2$.

Table 1. Summary of photovoltaic performance of different devices.						
Device	Voc [V] a)	J _{sc} [mA/cm²] b)	FF [%] ^{c)}	η [%] d)	R _{sh} [Ω cm²] ^{e)}	Rs [Ω cm²] ^{f)}
А	0.56	11.68	50.20	3.28	1177.7	160.1
В	0.64	12.75	52.41	4.27	2068.4	94.8

a) Open-circuit voltage, Voc; b) short-circuit current, Jsc; c) fill factor, FF; d) PCE, η ; The performances provided in the table are the champion ones; The average PCE values for five devices of A and B were 3.01% and 4.13%, respectively; The standard deviations were calculated to be ±0.27 and ±0.15, respectively; e) shunt resistance, Rsh; f) series resistance, Rs. Configurations: device A, ITO/ZnO/P3HT-PCBM (1:1, w/w)/V₂O₅/Ag; device B, ITO/ZnO/C-PCBB/P3HT-PCBM (1:1, w/w)/ V₂O₅/Ag.



Figure 7. Schematic configuration of inverted device architecture, ITO/ZnO/P3HT-PCBM (1:1, w/w)/V_2O₅/Ag without (Device A) and with (Device B) **C-PCBB** layer showing energy diagrams of the two localized heterojunctions at the interface.

8 days (Figure S4). The Device B (ITO/ZnO/**C-PCBB**/P3HT-PCBM/V₂O₅/Ag) retained >85% of its original PCE value after 8 days of exposure to ambient conditions. In sharp contrast, the PCE of device A (ITO/ZnO/P3HT-PCBM/V₂O₅/Ag) decayed very rapidly in just 2 days. This explicitly demonstrates the crucial role of **C-PCBB** interfacial layer in increasing the stability and lifetime of device B over device A. However, detailed device optimization and stability measurements under accelerated conditions are required, which is part of ongoing research in our lab.

Conclusions

We have successfully synthesized a cross-linkable fullerene derivative, PCBB and demonstrated its application as ETL in P3HT-PCBM based inverted polymer solar cells. PCBB act as 'cross-linkable PCBM' inheriting all the photophysical and electrochemical properties of PCBM. Thermal cross-linking of PCBB at 200 °C for 15 min directed the formation of solvent resistive films, which otherwise will get washed away during solution processing. Additionally, incorporation of C-PCBB interfacial layer reduced both roughness and aggregate growth in the active layer morphology. The performance of device fabricated with inverted configuration of ITO/ZnO/P3HT-PCBM/V₂O₅/Ag with C-PCBB interfacial layer showed ~25% improvement in PCE (4.27%) relative to the reference device (PCE = 3.28%). Our results confirm that incorporation of PCBB ETL facilitates cascade electron transport towards effective charge collection in PSCs. The strategies adopted in this work could be used in device fabrication for the construction of stable and efficient solar cells.

Experimental Section

Materials: The materials and reagents for synthesis were purchased from Sigma-Aldrich, Merck, and Spectrochem chemical suppliers. Regioregular P3HT (55 kDa) was purchased from Rieke Metal Inc. and PCBM (>99.5%) was obtained from Nano-C. These chemicals were used as received without further purification. Vanadium Pentoxide (V_2O_5)

(Baytron P VP AI 4083) was purchased from H. C. Stark and passed through a 0.45 μ m syringe filter before spin-coating. Patterned ITO was obtained from Ossila Ltd. All other reagents were purchased from Sigma-Aldrich and used as received. PCBA and Methylol benzoxazine were synthesized according to the reported procedures.

Synthesis of PCBB: To a solution of [6, 6]-Phenyl-C₆₁-butyric acid (50 mg. 0.056 mmol) in ODCB (5 mL) was added 4-dimethylaminopyridine (7 mg, 0.056 mmol), (16 mg, 0.084 mmol) and stirred for 10 min at 0 °C. Methylol benzoxazine (17 mg, 0.067 mmol) was added directly to the reaction mixture and stirred overnight at room temperature. The crude mixture was purified by column chromatography using toluene ($R_f = 0.6$) afforded brown colour solid in 24% yield (15 mg). ¹H NMR (500 MHz, CDCl₃), δ (ppm): 7.91 (t, 2H), 7.52 (m, 3H), 7.43 (m, 3H), 7.09 (t, 2H), 6.97 (m, 2H), 6.91 (t, 1H), 5.35 (s, 2H), 4.94 (s, 2H), 4.61 (s, 2H), 2.90 (t, 2H), 2.54 (t, 2H), 2.19 (m, 2H); ¹³C NMR (125 MHz, CDCl₃), δ (ppm): 172.96, 154.50, 150.69, 148.80, 148.26, 147.78, 145.84, 145.20, 145.15, 145.07, 145.04, 144.79, 144.67, 144.51, 144.40, 144.01, 143.76, 143.10, 143.00, 142.94, 142.91, 142.21, 142.18, 142.13, 142.11, 140.98, 140.75, 138.03, 137.57, 136.72, 132.11, 129.05, 128.45, 128.26, 128.14, 127.30, 121.62, 120.92, 118.99, 118.31, 79.86, 66.21, 51.84, 34.11, 33.62, 22.37; HRMS (m/z): [M]+ calculated for C₈₆H₂₅NO₃+, 1119.18; found, 1120.21 (M+H).

Device fabrication: The ZnO sol was prepared using a sol-gel procedure by dissolving zinc acetate dihydrate (C₄H₆O₄Zn.2(H₂O), 99.9%, 1.6 g) and monoethanolamine (HOCH₂CH₂NH₂, 99%, 0.045 g) in anhydrous 2-methoxyethanol (>99.8%, 0.96 mL) under vigorous stirring for hydrolysis reaction and aging for 3 h. The solar cell devices were fabricated under optimized conditions according to the modified reported procedure. The patterned indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in DIwater, chloroform and isopropyl alcohol for 10 min, respectively and subsequently dried in an oven overnight. After UV-ozone treatment for 15 min, nanosized ZnO thin films with a thickness of ca. 40-50 nm were spin-coated using the sol-gel precursor solution at 3000 rpm on top of the ITO substrate. The films were sintered at 200 °C for 30 min in air. During this process the precursor converts to ZnO gel and forms a transparent thin film of ZnO nanoparticle. For device fabricated with C-PCBB interlayer (device B), an ODCB solution containing PCBB (5 mg/mL) was spin-cast on the ZnO film to form a thin film with a thickness of ca. 10 nm. Subsequently, the as-cast film was heated at 200 °C for 15 min for thermal cross-linking in the glove box. For devices A and B, a ODCB solution containing a mixture of P3HT-PC61BM (1:1, w/w) was then spincast to form a 130 nm thin film on top of the ZnO (Device A) and C-PCBB (Device B) thin film, respectively. Both the devices were thermally annealed at 120 °C for 10 min in the glove box followed by spin-coating vanadium pentoxide with a thickness of ca. 40 nm and then heated at 120 °C in the glove box. Finally, the top electrode of Ag film (100 nm-thick), was evaporated thermally at a pressure below 10⁻⁶ torr. Devices without encapsulation were characterized in ambient condition. The active area used for the measurement was 0.1 cm².

Characterization and measurements: ¹H (500 MHz) and ¹³C NMR (125 MHz) spectra were measured on a Bruker Avance DPX spectrometer. Chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) ($\delta_{\rm H} = 0$ ppm) or the solvent residual signal (CDCl₃: $\delta_{\rm C} = 77.00$ ppm) as an internal reference. The resonance multiplicity is described as s (singlet), d (doublet), t (triplet) and m (multiplet). High resolution mass spectral (HRMS) analysis was performed on a Thermo Scientific Q Exactive Hybrid Quadrupole-Orbitrap electrospray ionization mass spectrometer (ESI-MS) instrument. Infrared spectra were recorded in the diffused reflectance mode in the solid state (KBr) using Shimadzu IR Prestige-21 Fourier Transform

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Infrared Spectrophotometer. All experiments were carried out using spectroscopic grade solvents at room temperature (25 \pm 1 °C) unless otherwise mentioned.

The UV/Vis absorption spectra were recorded on a Shimadzu UV-2600 Spectrophotometer, Fluorescence spectra were collected using a SPEX-Fluorolog F112X Spectrofluorimeter equipped with a 450 W Xenon arc lamp. Thermogravimetric analyses were carried using TG/DTA-6200 instrument (SII Nano Technology Inc.) by heating the sample from room temperature to 700 °C at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. Curing temperature was measured using differential scanning calorimeter (Perkin-Elmer Pyris 6 DSC instrument) in sealed aluminium pans by heating the sample from 20 °C to 250 °C at a rate of 10 °C min⁻¹. The square wave voltammetry was done on CV, BASI CV-50W instrument using thin film coated glassy carbon as working electrode at room temperature in the presence of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) as supporting electrolyte, Ag/AgCl electrode as reference electrode and platinum wire as counter electrode in acetonitrile under argon atmosphere with a scan rate of 50 mV/s. A BRUKER MULTIMODE AFM operating with a tapping mode regime was used to record AFM images under ambient conditions. Micro-fabricated TiN cantilever tips (NSG10) with a resonance frequency of 299 kHz and a spring constant of 20-80 Nm⁻¹ were used. AFM section analysis was done offline. Samples for the imaging and roughness measurements were prepared as explained in device fabrication section under ambient conditions. The thickness of various films was measured using Bruker Stylus Profilometer (Dektak XT). The current densityvoltage (J-V) characteristics were measured with a Keithley 2400 source-meter under AM 1.5G (100 mWcm⁻²) solar simulator. The shunt and series resistance of the devices was calculated through slope of J-V curve at J_{sc} and V_{oc} respectively.

Acknowledgements

The financial support from Council of Scientific and Industrial Research (TAPSUN, NWP-54) and Department of Science and Technology, Government of India (Ramanujan Fellowship Grant RJN-19/2012; GAP 1366) are gratefully acknowledged. S.K.V. and R.R. acknowledges University Grant Commission (UGC, Government of India) and CSIR respectively, for Research Fellowship.

Keywords: cross-linking • electron transport • fullerenes • photovoltaics• solar cells

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Table of Contents

FULL PAPER

A cross-linkable fullerene derivative PCBB, functionalized with benzoxazine moiety resulted crosslinked, solvent resistive adhesive film upon heat triggered ring opening polymerisation. The fabrication of inverted bulk hetero junction solar cell using cross-linked PCBB as electron transport layer achieved 25% enhancement in the power conversion efficiency compare to the reference device.



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A Cross-Linkable Electron Transport Layer Based on a Fullerene– Benzoxazine Derivative for Inverted Polymer Solar Cells

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