Rational synthesis of a polymerizable fullerene–aniline derivative: study of photophysical, morphological and photovoltaic properties[§]

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MS received 11 August 2018; revised 28 August 2018; accepted 30 August 2018; published online 20 September 2018

Abstract. This paper describes the synthesis of a polymerizable, aniline appended fullerene derivative, 3-aminobenzyl-phenyl- C_{61} -butyrate (**PCBAn**) and its corresponding polymer (**P-PCBAn**), and detailed photophysical and morphological analysis towards application as an acceptor in polymer solar cells (BHJ-PSCs). The poly-3-aminobenzyl-phenyl- C_{61} -butyrate (**P-PCBAn**), having a substituted polyaniline (PANI) skeletal structure, was synthesized *via* $FeCl_3$ oxidative polymerisation of PCBAn in its non-conducting leucoemeraldine state. HOMO and LUMO energies estimated using optical and electrochemical techniques revealed upshifted LUMO levels for **PCBAn** (−3.68 eV, $\Delta E = 0.1$ eV) and **P-PCBAn** (−3.66 eV, $\Delta E = 0.12$ eV) compared to the parental fullerene derivative, **PCBM** (−3.78 eV). The morphologies of **PCBAn** and **P-PCBAn** individually and in polymer blends with **P3HT** were investigated using AFM and TEM analysis, which showed nanoflake-like aggregates for **P3HT/PCBAn** and a favourable interconnected nanonetwork structure for **P3HT/P-PCBAn**. The wide angle X-ray scattering (WAXS) studies of **PCBAn** films drop-cast from THF/water (3:7) mixture and **P-PCBAn** films drop-cast from 1,2-dichlorobenzene exhibited plane reflections of lamellar mesophases with d-spacing of 3.4 nm and 3 nm for **PCBAn** and **P-PCBAn**, respectively. The fluorescence quenching experiments with **P3HT** indicated efficient electron transfer from **P3HT** to **P-PCBAn** when compared to **PCBAn**. The fabrication of an inverted BHJ-PSC device using **PCBAn** and **P-PCBAn** as an acceptor in combination with **P3HT** showed PCE of 0.9% and 1.1%, respectively, showing considerable enhancement in the case of the polymeric acceptor. The polymeric acceptor and the rational design strategy used here could open up new opportunities in the PSC device fabrication.

Keywords. Fullerene; oxidative polymerisation; self-assembly; polymer blends; nanostructures; polymer solar cells.

1. Introduction

Tremendous research has been commenced in the last two decades in the area of bulk heterojunction (BHJ) polymer solar cells (PSCs) because of its potential future application as an easy processable, flexible, lightweight, inexpensive and transportable energy source.^{1,2} During this period, Poly(3-hexylthiophene) (**P3HT**) donor and the phenyl- C_{61} -butyric acid methyl

ester (**PCBM**), acceptor polymer blends came out to be one of the most well-studied systems and widely used as a standard for comparing the power conversion efficiency (PCE) of PSCs.³ Along with device architecture, processability and annealing with different solvent composition lead the **P3HT-PCBM** system to reach PCE of greater than 5%.⁴ Also, the development of various polymeric donor systems led to the record high PSC efficiency of >10%.⁵ For

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§Dedicated to Professor M V George on the occasion of his 90th Birth Anniversary.

Electronic supplementary material: The online version of this article (<https://doi.org/10.1007/s12039-018-1547-8>) contains supplementary material, which is available to authorized users.

example, Yang Yang *et al.*, have developed a low band gap polymer poly[2,7-(5,5-bis-(3,7-dimethyloctyl)-5H-dithieno[3,2-b:2',3'-d]pyran)-alt-4,7-(5,6-difluoro-2,1,3-benzothiadiazole)](PDTP-DFBT) with a PCE of 8.1% in combination with PC₇₁BM as an acceptor with inverted configurations and a highest PCE of 10.2% with tandem device architecture.⁶ Yongfang Li *et al.*, reported remarkable PCE of 7.4% using vertically aligned cross-linked fullerene derivative as electron transport layer in **P3HT**: fullerene based system.⁷ Compared to the tedious synthetic process of polymer functionalization, rationally modifying the **PCBM** acceptor part for achieving improved charge transport properties became a strategy of interest in the scientific community.⁸ Many research groups approached smart modification of **PCBM** by substituting visible absorbing moieties,^{9–12} self-assembling units,^{13,14} tuning the Lowest Unoccupied Molecular Orbitals (LUMO)^{15,16} and increasing the electron mobility^{17,18} in order to achieve higher PCE by increasing electron transport properties. Also, up-shifting the LUMO of the acceptor is an alternative for solving the puzzle of increasing the V_{oc} of the active layer. For example, Indene-C₆₀ bisadduct (ICBA) and Indene-C₇₀ bisadduct (IC₇₀BA) having 0.17 eV and 0.19 eV higher LUMO energy levels respectively, than **PCBM** are excellent acceptors for the **P3HT**-based PSCs due to the electron-rich character of indene and the bisadduct effect.^{19,20}

Out of many key parameters for the successful PSC device, active layer morphology plays a crucial role and it is extremely necessary to obtain the bicontinuous interpenetrating architecture for better device performance.²¹ Through systematic study many research groups adopted different strategies to optimize the morphology of polymer blend by varying the ratio and concentration of the donor-acceptor systems, choosing binary or ternary solvent, thermal annealing, solvent annealing and using appropriate solvent additives.^{22,23} Self-assembling nature of fullerenes also has been extensively used to organize them with polymer donor into one-dimensional nanofibres or nanonetwork structures.²⁴ These soft techniques tend to give better nanoscale morphology and good phase separation. But, in actual solar cells, the nanostructures undergo many heat-cool cycles over the time. As a result, the thermodynamically unstable nanostructures tend to aggregate into macroscopic phase-separated structures and deteriorate device performance with time.²⁵ Since fullerenes have a higher tendency of aggregation compared to polymer donor, **PCBM** in the active layer is usually responsible for the formation of needle-like structures upon ageing. One way to overcome these problems is to arrest the morphology by cross-linking donor-donor,

donor-acceptor or acceptor-acceptor units.^{26,27} Following this strategy, many cross-linkable units such as acetylene, styrene, oxetane, and epoxide have been attached to fullerene part in the design of new morphologically stable fullerene-based acceptors.^{28–31} But in many cases, post-cross-linking methods fails to form monodisperse films and suffer from poor charge separation due to the presence of insulating cross-linkable groups.³²

These limitations signify the importance of new polymeric fullerene acceptors which in combination with the polymer donor can give resultant large interfacial area, efficient exciton dissociation and well-separated pathways for free charge transport across the active layer. Most of the polymer-based materials have the intrinsic one-dimensional nanofibrous structure, easy polymerization conditions and excellent thermal stability. In this context, developing polyfullerene without affecting the core fullerene structure is of great scientific relevance for the optoelectronic applications.²⁷ Basically, there are two types of fullerene polymers known so far.³³ One is pearl necklace type, containing fullerene as the main chain polymer. Secondly, charm bracelet type polyfullerenes containing fullerenes in the pendent chain. Many of such reported polyfullerenes have drawbacks such as tedious synthetic procedures, large insulating part in the substitution, solubility issues, and lack of one-dimensional nanostructures.³⁴ Therefore, there is a need for the design of polyfullerene having facile monomer to polymer conversion, good miscibility with the donor counterpart, synthetic easiness and possessing better optoelectronic properties than parental **PCBM**.

Out of numerous polymerizable groups available in the polymer chemistry arena, the polyaniline (**PANI**) is one of most extensively studied and cost-effective polymer which is known for its high conductivity, synthetic easiness and good electrochemical properties.^{35,36} Synthesis of **PANI** from its monomers by various methods such as oxidative polymerisation using APS or FeCl₃ both in the aqueous and organic medium are known.³⁷ **PANI** can exist in three different oxidation states *viz.* the emeraldine (green form), leucoemeraldine (yellow form) and the pernigraniline oxidation state (black form).^{38,39} These synthesized polymers often tend to give networked nano structure with improved electronic properties due to which they can be better candidates for the design of polyfullerenes for the photovoltaic applications.⁴⁰ Fullerene-**PANI** composites and copolymerization of single fullerene unit with **PANI** tags have been previously studied.^{36,41,42}

Herein, we report the synthesis of a novel **PCBM** derivative with covalently modified aniline moiety,

3-aminobenzyl-[6,6]-phenyl- C_{61} -butyrate ester (**PCBAn**) and its polymer, **P-PCBAn**. Detailed characterization of **PCBAn** and **P-PCBAn** along with photophysical and morphological analysis were undertaken with a view to understand their potential for applications in PSCs. The square wave voltammetry revealed the relatively upshifted LUMO levels of **P-PCBAn** compared to **PCBAn** and parental **PCBM**. Also, **P3HT**-fluorescence showed efficient quenching in the presence of **PCBAn** and **P-PCBAn** indicating efficient electron transport properties. The films of **P-PCBAn** exhibited networked nanostructure with enhanced absorption in the visible region compared to its monomer counterpart. The fabrication of BHJ-PSC device was demonstrated using **P3HT**: **P-PCBAn** and **P3HT**: **PCBAn** polymer blends which revealed relatively higher device performance (1.1%) for **P-PCBAn** compared to **PCBAn** (0.9%).

2. Experimental

2.1 Materials and methods

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 μm syringe filter before spin-coating. Patterned ITO was obtained from Ossila Ltd. All other reagents were purchased from Sigma-Aldrich and used as received. ^1H (500 MHz) and ^{13}C NMR (125 MHz) spectra were measured on a Bruker Avance DPX spectrometer. Chemical shifts are reported in parts per million (ppm) using tetramethylsilane (TMS) ($\delta_{\text{H}} = 0$ ppm) or the solvent residual signal (CDCl_3 : $\delta_{\text{C}} = 77.00$ 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 Infrared Spectrophotometer. All experiments were carried out using spectroscopic grade solvents at room temperature (25 ± 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. Fluorescence Lifetime measurements were carried out using IBH (model 5000DPS) time-correlated single photon counting system (TCSPC). The pulse width of the light source used was 200 ps. The lifetime values were obtained using DAS6 decay

analysis software. The quality of fit has been judged by the fitting parameters such as χ^2 (<1.1) as well as the visual inspection of the residuals. 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 (TBAPF_6) 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 N m^{-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 profilometer. The current density-voltage (J–V) characteristics were measured with a Keithley 2400 source-meter under AM 1.5G (100 mW cm^{-2}) solar simulator.

2.2 AFM/TEM sample preparations

Samples for AFM analysis were prepared by drop-casting 10 μL solution of **PCBAn** (1 mg/mL, THF/ H_2O , 3:7), **P-PCBAn** (1 mg/mL in ODCB) onto freshly cleaved mica sheet under ambient conditions and were dried under air. In case of the polymer blend, the samples were prepared as discussed in device fabrication section. A BRUKER MULTIMODE AFM operating with a tapping mode regime was used to record AFM images under ambient conditions. Micro-fabricated TiN cantilever tips (NT-MDT-NSG series) with a resonance frequency of 299 kHz and a spring constant of 20 to 80 N m^{-1} were used. AFM section analysis was done offline. TEM samples were prepared by drop casting 10 μL solution of the sample on the top of the carbon-coated copper grid (400 mesh). The samples were allowed to adsorb on the grid overnight at ambient conditions. TEM analysis was performed with a JEOL 100 kV high-resolution transmission electron microscope. The accelerating voltage of the TEM was 100 kV and the beam current was 65 A. Samples were imaged with a Hamamatsu ORCA CCD camera.

2.3 BHJ device fabrication

The ZnO sol was prepared using a sol-gel procedure by dissolving zinc acetate dihydrate ($\text{C}_4\text{H}_6\text{O}_4\text{Zn} \cdot 2\text{H}_2\text{O}$), 99.9%, 1.6 g) and monoethanolamine ($\text{HOCH}_2\text{CH}_2\text{NH}_2$, 99%, 0.045 g) in anhydrous 2-methoxyethanol (> 99.8%, 0.96 mL) under vigorous stirring for hydrolysis reaction and ageing 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 DI-water, chloroform and isopropyl alcohol for 10 min, respectively and subsequently dried in an oven overnight. After

Scheme 1. Synthetic scheme for **PCBA n**. EDC: 1-ethyl-3-(3-(dimethylamino)propyl) carbodiimide, DMAP: 4-(dimethylamino)pyridine, ODCB: 1,2-dichlorobenzene, TFA: Trifluoroacetic acid.

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 devices A and B, a ODCB solution containing a mixture of **P3HT/PCBA n** (1:1, w/w) (Device A) and **P3HT/PCBA n** (1:1, w/w) (Device B) was then spin-cast to form a 130 nm thin film on top of the ZnO 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 and were optimized by testing approximately 10–12 cells.

3. Results and Discussion

3.1 Synthesis and oxidative polymerization of **PCBA n**

The synthesis of 3-aminobenzyl-[6,6]-phenyl-C₆₁-butyrate ester (**PCBA n**) was achieved by following

Scheme 1. Acid hydrolysis of **PCBM** afforded [6,6]-Phenyl-C₆₁-butyric acid (**PCBA**) in quantitative yield which upon EDC mediated esterification reaction with tert-butyl-3-(hydroxymethyl)phenylcarbamate gave the corresponding Boc protected **PCBA n** derivative in 57% yield. Further deprotection of Boc with trifluoroacetic acid, followed by neutralization with sodium bicarbonate resulted in **PCBA n** in quantitative yield. Tert-butyl-3-(hydroxymethyl)phenylcarbamate was separately obtained in moderate yields by the Boc protection reaction of (3-aminophenyl)methanol and di-tert-butyl-dicarbonate. All the intermediates and final compounds were well-characterized by various analytical and spectroscopic techniques (see Supporting Information). For example, ¹H NMR spectra of **PCBA n** showed characteristic proton signals corresponding to the methyl protons of the benzylamine group at 5.35 ppm and 4.94 ppm and the alkyl protons in the range of 2.1–2.9 ppm. In the ¹³C NMR, we have observed chemically distinct carbon signals which can be assigned as per the structure of **PCBA n**. The FT-IR spectrum of **PCBA n** showed a peak at 1684 cm⁻¹ corresponding to carbonyl stretching frequency. UV-Visible absorption spectrum revealed characteristic absorption of functionalized fullerene at 328 nm. The MALDI

analysis showed the exact mass of **PCBAn** at 1001.31. These spectral and analytical techniques confirm the successful coupling of the PCBA and benzoxazine moieties.

Oxidative polymerisation of aniline or anilinium salts can be easily carried out using APS or FeCl_3 reagents, yielding the corresponding conductive polymer with defined nanostructures.^{43,44} Since the **PCBAn** have the aniline moiety, the oxidative polymerisation reaction may lead to the successful grafting of fullerene on polyaniline (**PANI**) backbone. The oxidative polymerization of **PCBAn** to obtain **P-PCBAn** was conducted in chloroform in the presence of FeCl_3 under reflux conditions, which yielded the polymer as a brown solid residue in quantitative yields. The solid thus obtained was subsequently washed with chloroform and water to remove unreacted monomers and FeCl_3 to get **P-PCBAn** in 60% yield. The formation of **P-PCBAn** polymer was further characterized through ^1H NMR, FT-IR and UV-Visible absorption spectroscopy (See Supporting Information).

A typical FT-IR spectrum of **PCBAn** and **P-PCBAn** were compared in Figure S1a (Supplementary Information). The **P-PCBAn** exhibited similar spectral characteristics as that of **PCBAn** monomer in the fingerprint region but showed a broad peak centered around 3345 cm^{-1} , characteristic of $-\text{NH}$ stretching vibration, confirming successful polymerization. As discussed, the polyaniline can exist in three different oxidation states such as highly oxidized state penigraniline, conductive state emeraldine and non-conductive leucoemeraldine state.^{45,46} A comparison of the UV-Vis absorption

spectra of **PCBAn** and **P-PCBAn** with reported **PANI** structures was made to understand the oxidation states of **PANI** formed during the oxidative polymerisation (Figure S1b, Supplementary Information). **PCBAn** in THF showed characteristic absorption peak at around 328 nm whereas **P-PCBAn** displayed an additional broad band, at 365 nm. Based on the absorption properties in comparison with reported **PANI** structures, the synthesized **P-PCBAn** is assigned to have non-conductive leucoemeraldine state of **PANI** as polymer backbone.⁴⁷ Matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) studies of **PCBAn** and **P-PCBAn** were carried out using 2,5-dihydroxybenzoic acid as a matrix material (Figure S2, Supplementary Information). **PCBAn** showed typical m/z molecular ion peak at 1120 whereas **P-PCBAn** exhibited m/z ion peak corresponding to M^+ , $2(M^+ + K)$ and $3(M^+ + K)$. The lack of higher mass peak might be due to the difficulty of polymers in being desorbed/ionized without decomposing. Similar observations were earlier reported for the construction of polyfullerene from photochemical reactions of fullerene clusters.⁴⁸

3.2 Electrochemical studies

We compared the reduction potentials of **PCBAn** and **P-PCBAn** with **PCBM** using Square Wave Voltammetry (Figure 1a) conducted on glassy carbon as a working electrode in the presence of 0.1 M TBAPF_6 as supporting electrolyte, Ag/AgCl electrode as a reference electrode and a platinum wire as a counter electrode in acetonitrile, calibrated by ferrocene ($E_{1/2}(\text{ferrocene}) =$

Figure 1. (a) Square wave voltammetry of **PCBAn**, **P-PCBAn** and **PCBM** measured in acetonitrile at a scan rate of 0.1 V/s under N_2 , 0.1 M Bu_4NPF_6 electrolyte with Pt (working electrode), Pt wire (counter electrode), Ag/AgNO_3 (reference electrode). (b) HOMO–LUMO energy level diagram of fullerene derivatives, **PCBM**, **PCBAn**, **P-PCBAn** and **P3HT**.²⁹ The energy levels were drawn relative to the vacuum level.

0.45 V vs. Ag/AgCl). The first reduction potentials of **PCBM**, **PCBAn** and **P-PCBAn** were observed at -0.57 V, -0.67 V and 0.69 V, respectively. The LUMO energy levels were calculated from reduction potentials using the formula,

$$E_{\text{LUMO}} = -e[4.8 + E_{\text{red}} - 0.45] \text{ eV} \quad (1)$$

Where, E_{red} is the reduction potential vs Ag/AgCl electrode using ferrocene as the standard ($E_{1/2}(\text{ferrocene}) = 0.45$ V vs. Ag/AgCl).²⁰ The LUMO energy levels of **PCBM**, **PCBAn** and **P-PCBAn** were found to be -3.78 eV, -3.68 eV and -3.66 eV, respectively. The HOMO energy levels were calculated using optical band gap (E_{gap}) using the formula $E_{\text{gap}} = \text{HOMO-LUMO}$ and were found to be -5.5 eV, -5.38 and -5.34 eV, respectively. The reduction potentials, HOMO-LUMO energy levels and the optical band gap of **PCBAn**, **P-PCBAn** and **PCBM** were listed in the Table S1 (Supplementary Information).

The observed changes in the reduction potentials indicate slight modification of the electronic energy levels in case of synthesized fullerene derivatives compared to **PCBM**. **PCBAn** and **P-PCBAn** exhibited upshift of LUMO energy levels by 0.10 eV and 0.12 eV, respectively compared to **PCBM**. This could be due to the cofacial pi-orbital interaction between the C_{60} and the aniline moieties in **PCBAn** and **P-PCBAn**.¹⁸ The pictorial representation of HOMO-LUMO levels of **PCBM**, **PCBAn**, **P-PCBAn** along with donor **P3HT** were depicted in the Figure 1b. From this, it is clear that the rise in LUMO energy levels can help easy charge transport at the **P3HT** donor and fullerene acceptor interface. Hence, the relative upshift of **PCBAn** and **P-PCBAn** LUMO levels serves them as better electron acceptors rather than **PCBM**.

3.3 Photophysical and morphological studies

A challenging task in fullerene chemistry is the construction of one-dimensional nanostructure, which is advantageous for many optoelectronic applications.^{49,50} In the present case, photophysical and morphological behaviour of **P-PCBAn** might differ from monomeric **PCBAn** due to the inherent polymeric nature of the former. Moreover, the fullerene derivatives are known to self-assemble into various shapes in binary solvents. Hence, we investigated the photophysical and morphological properties of self-assembled **PCBAn** in THF- H_2O mixtures and **P-PCBAn** in 1,2-dichlorobenzene. Absorption spectra of **PCBAn** in THF ($10 \mu\text{M}$) showed characteristic fullerene absorption peaks at 258 nm

and 328 nm (Figure S3a, Supplementary Information). The solvent polarity was changed by the fraction of water in the solvent mixture and we observe no significant changes upto a 1:1 THF/ H_2O mixture. At higher water fractions, a new band formation around 450 nm with concomitant hypochromism at 258 nm absorption band was observed. In THF/ H_2O (3:7) mixture, a bathochromic shift of 16 nm and 10 nm for the 258 nm and 328 nm bands, respectively accompanied by pronounced 450 nm absorption band was observed. This might be attributed to the aggregation of **PCBAn** monomers due to the solvophobic effect in which fullerene core tend to come closer with more hydrophilic aniline group project outwards. To understand the reversibility of these aggregates, temperature dependent UV-visible absorption studies were carried out (Figure S3b, Supplementary Information). Upon increasing the temperature from 25°C to 85°C , the absorption bands at 274 nm and 338 nm undergo a hypsochromic shift to their initial value with concomitant disappearance of the 450 nm band. These results indicate the thermal reversibility of **PCBAn** aggregates in THF/ H_2O (3:7) mixture.

The self-assembly behaviour was further investigated through AFM and TEM analyses to understand the morphology of **PCBAn** aggregates. AFM analysis of a drop cast film of **PCBAn** ($10 \mu\text{M}$) from THF/ H_2O (3:7) mixture on freshly cleaved mica ($10 \mu\text{L}$) exhibited particles of around 100 – 150 nm width (Figure 2a). TEM analysis of **PCBAn** drop-cast on a carbon-coated copper grid revealed particles with size ~ 150 nm similar to that observed in AFM (Figure 2b). Zoomed images of the particle clearly showed wrinkled flake like nanostructures with multiple layers at the edges (Figure 2c). DLS experiments of the same solution which was used for the microscopic studies revealed an average hydrodynamic diameter of 125 nm with good correlogram (Figure 2d). These morphological studies reveal that **PCBAn** in the presence of binary solvent mixture (THF/ H_2O) form particle-like aggregates.

AFM analysis of drop cast film of **P-PCBAn** (1 mg/mL , 1,2-dichlorobenzene) on mica and analyzed under AFM (Figure 3a) revealed an interconnected nanonetwork structure with a diameter of around 50 – 100 nm. HR-TEM analyses of the same solution further confirmed the nanonetwork structure (Figure 3b). Since **PANI** polymers are known to give nanofibre network structure, the observed nanonetwork might consist of polyaniline main chain with pendent fullerene moieties. DLS experiment revealed the hydrodynamic particle size of 190 nm with good correlogram which was in line with AFM and TEM results (Figure 3c and d). The **PCBAn** in 1,2-dichlorobenzene at similar

Figure 2. (a) AFM height image; (b) TEM image of **PCBA n** in THF/H₂O (3:7) mixture and (c) zoomed portion showing wrinkled flake like nanostructure. (d) DLS size distribution of **PCBA n** (inset: corresponding correlogram).

concentrations did not show any nanostructures, as it is highly soluble and tend to exist as a monomer.

3.4 Wide angle X-ray scattering (WAXS) studies

The wide angle X-ray scattering (WAXS) studies of **PCBA n** cast film in THF/water (3:7) mixture and **P-PCBA n** in 1,2-dichlorobenzene was carried to understand the packing of molecules in the self-assembled nanostructures. **PCBA n** showed well-defined peaks at two theta values of 2.55, 7.85, 10.3 degrees corresponding to (001), (003), (004) plane reflections of lamellar mesophases (Figure 4a).^{51,52} The broad peak from 15–25 degree corresponds to alkyl chain interactions with d-spacing of 3.4 nm which is consistent with the bilayer lamellar mesophases model shown in Figure 4b where fullerene core point inwards and alkyl chain project outwards.⁵⁰ **P-PCBA n** in ODCB also showed similar but slightly shifted crystalline peaks at two theta value of 2.83, 5.81, 8.54, 10.48 degree corresponding to (001), (002), (003), (004) plane reflections of lamellar mesophases with d-spacing of 3 nm (Figure 4c). The decrease in the d-spacing is

associated with the covalent linkage of **PCBA n** monomers in **P-PCBA n**, decreasing the distance between the adjacent C₆₀ moieties without losing crystallinity as schematically represented in Figure 4d. This XRD study is in agreement with morphology obtained from AFM and TEM analyses and indicates a type of directed self-assembly through hydrophobic-hydrophilic balance in aqueous or solvophobic-solvophilic balance in non-aqueous media.

3.5 Solution state absorption and emission studies

To further investigate the acceptor ability of the **PCBA n** monomer and **P-PCBA n** polymer, fluorescence quenching studies were carried out in the presence of **P3HT** polymer donor. The fluorescence emission spectra of **P3HT** solution in 1,2-dichlorobenzene were measured with different concentrations of **PCBA n** or **P-PCBA n** and the results are summarized in Figure S4 (Supplementary Information). Pure **P3HT** donor in 1,2-dichlorobenzene solution displayed a fluorescence emission maximum at 583 nm. The fluorescent emission intensity decreased with increasing addition

Figure 3. (a) AFM height image; (b) TEM image; (c) DLS size distribution profile and (d) corresponding correlogram of **P-PCBAn** in 1,2-dichlorobenzene.

Figure 4. WAXS pattern of (a) self-assembled **PCBAn** in THF/H₂O (3:7) and (b) **P-PCBAn** in 1,2-dichlorobenzene. Proposed schematic model for the nanostructure formed by the self-assembly of (c) **PCBAn** and (d) **P-PCBAn**.

Figure 5. (a) Stern-Volmer plot obtained from the fluorescence quenching between **P3HT** donor with **PCBA** and **P-PCBA** acceptor; (b) Photograph of (i) **P3HT**, (ii) **P3HT:PCBA** and (iii) **P3HT:P-PCBA** (1 mg/mL each) under UV light (365 nm) showing difference in quenching behaviour of monomer and polymeric acceptors.

of fullerene derivatives. The fluorescence of **P3HT** underwent 22% quenching in the presence of 40 equivalents of **PCBA** (Figure S4a, Supplementary Information). On the other hand, it exhibited two-fold higher percentages of quenching (57%) with the same equivalents of **P-PCBA** (Figure S4b and Figure S6 in Supplementary Information). In order to understand the quenching efficiency of the fullerene acceptors, we used a Stern-Volmer quenching plot using the equation.

$$I_0/I = 1 + K_{sv}[Q] \quad (2)$$

Where, I_0 and I are the measured fluorescence intensities in the absence and presence of the quencher, respectively, K_{sv} is the Stern-Volmer quenching constant, and $[Q]$ is the concentration of the quencher. The Stern-Volmer equation provides useful information on the intermolecular quenching process. Stern-Volmer quenching plots of **P3HT** donor in the presence of **PCBA** and **P-PCBA** as the quenchers are shown in Figure 5a. The **P3HT-PCBA** displayed a straight line indicating dynamic quenching behaviour between the donor-acceptor molecules with a Stern-Volmer constant of $K_{sv} = 4.3 \times 10^3 \text{ M}^{-1}$, a value similar to that reported for **P3HT-PCBM** donor-acceptor pair. However, the plot corresponding to **P3HT-P-PCBA** combination exhibited upward curvature representing the existence of both static and dynamic quenching behaviour.⁵³ This can be correlated with a binding affinity between the fluorophore and the quencher. For instance, **P-PCBA** exists as a networked structure in the solution and hence it can undergo better pi-stacking with **P3HT**, accounting for the static quenching along with the usual collisional quenching. However, **PCBA** exists in the molecularly

dissolved form in 1,2-dichlorobenzene and could cause quenching of **P3HT** fluorescence mainly through collision. The higher quenching behaviour of **P-PCBA** can be visually identified by comparing the UV light illuminated solutions of **P3HT**, **P3HT:PCBA** and **P3HT:P-PCBA** as shown in Figure 5b.

Lifetime studies were carried out to get further insight into the quenching behaviour of **P3HT** donor in the presence of **PCBA** and **P-PCBA** acceptors (Figure S5a, in Supplementary Information). The relative lifetime values upon excitation with 375 nm laser were summarized in Figure S5b (Supplementary Information). The **P3HT** showed the lifetime values of 0.53 ns with single exponential decay. In the presence of **PCBA** (1:40 equivalents), the lifetime reduced to 0.49 ns due to the dynamic quenching. While, **P3HT:P-PCBA** (1:40 equivalents) experienced bi-exponential decay with lifetime of 0.21 ns (24.2%) and 0.53 ns (75.8%) with an average lifetime of 0.45 ns. The values correspond to the different extent of fluorophore-quencher interactions in the **P3HT-P-PCBA** blends with ideal static quenching lead to non-fluorescent complexes.

3.6 Solid state absorption and emission studies

Solid state UV-visible absorption and fluorescence quenching studies were also carried out for the donor-acceptor polymer blend active films. The pristine **P3HT** showed an intense visible absorption with maxima at 515 nm and 553 nm (Figure 6a). The shoulder band at 603 nm indicates the crystallinity of **P3HT** in the film state which was almost unchanged in the presence of **PCBA**.⁵⁴ In the case of **P3HT:P-PCBA** film the shoulder band underwent ~7 nm bathochromic

Figure 6. Solid state (a) UV-Visible absorption and (b) emission spectral profiles of **P3HT**, **P3HT:PCBAAn** and **P3HT:P-PCBAAn** polymer blend films, $\lambda_{\text{exc}} = 600$ nm.

Figure 7. AFM phase images of (a) **P3HT:PCBAAn** and (b) **P3HT:P-PCBAAn** polymer blend films and (c-d) corresponding cartoon representation of the self-assembly process.

shift which might be attributed to the self-assembling behaviour of **P-PCBAAn** polyfullerene with **P3HT** polymer.²² Moreover, the pristine **P3HT** film showed an emission maximum at 720 nm upon excitation at 600 nm and the fluorescence intensity was decreased upon blending with acceptors (Figure 6b). Fluorescence emission intensity in **P3HT:PCBAAn** blend film underwent 34% quenching at 720 nm relative to **P3HT**. Whereas in the case of **P3HT:P-PCBAAn**, a 67% quenching was observed. This increased fluorescence quenching of **P3HT** in the presence of **P-PCBAAn** is in line with the

solution state quenching results and confirms that the charge transfer process is more efficient in the **P3HT:P-PCBAAn** blend system compared to **P3HT:PCBAAn**.

3.7 Morphological analysis of polymer blends

The morphology of the resultant polymer blend plays important role in determining the performance of polymer solar cells. In this regard, AFM analysis was performed to understand the resultant morphology of the **P3HT:PCBAAn** and **P3HT:P-PCBAAn** polymer

Figure 8. J-V curves of (a) device A and (b) device B under AM 1.5 G illumination.

blends film after thermal annealing at 120 °C. AFM phase image of the **P3HT: PCBA**n polymer blend film revealed the formation of spherical aggregates whereas **P3HT: P-PCBA**n blend showed interpenetrating network structures under similar conditions (Figure 7a and b). The particle-like nanostructures of **P3HT: PCBA**n might be because of the aggregation of **PCBA**n monomer during the thermal annealing process (Figure 7c). The intrinsic networked nanostructure of **P3HT** and **P-PCBA**n rendered the formation of self-assembled interpenetrated nanonetwork architecture by means of various noncovalent interactions (Figure 7d). Therefore, the morphological analysis of the polymeric blend films confirms the well-ordered interaction of **P3HT** with polymeric **P-PCBA**n than monomeric **PCBA**n.

3.8 Photovoltaic properties

BHJ-PSC devices were fabricated with inverted configuration ITO/ZnO/**P3HT: PCBA**n/ V_2O_5 /Ag (Device A) and ITO/ZnO/**P3HT: P-PCBA**n/ V_2O_5 /Ag (Device B) using **PCBA**n and **P-PCBA**n as active layer electron acceptors. Device A and B were prepared by spin-coating a mixture of **P3HT/PCBA**n (1:1, w/w) and **P3HT/P-PCBA**n (1:1, w/w) respectively, from 1,2-dichlorobenzene to form a 130 nm thin film on ZnO coated ITO substrates. Current-voltage characteristics were measured using a Keithley under the irradiation of AM 1.5G solar simulator (Figure 8). Under identical fabrication conditions, device A showed a PCE of 0.9% whereas in the **P3HT: P-PCBA**n device

B, substantially improved PCE of 1.1% observed (Table 1). The increased PCE of Device B is mainly because of the simultaneous enhancement in the short-circuit current (J_{sc}) from 4.23 mA cm^{-2} in device A to 9.57 mA cm^{-2} device B and fill factor (FF) from 40.5 to 43.81. The overall PCE analysis of the inverted PSC devices using **P3HT: PCBA**n and **P3HT: P-PCBA**n

Table 1. Definitions: open-circuit voltage, V_{oc} ; short-circuit current, J_{sc} ; fill factor, FF; PCE, η ; Configurations: device A, ITO/ZnO/**P3HT: PCBA**n/ V_2O_5 /Ag and device B, ITO/ZnO/**P3HT: P-PCBA**n/ V_2O_5 /Ag.

Device	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF (%)	PCE (%)
A	0.53	4.23	40.5	0.91
B	0.26	9.57	43.81	1.1

active layer confirms that **P-PCBA**n is an efficient electron acceptor than **PCBA**n. The observed lower PCE of both devices in comparison to reported **P3HT: PCBM** device might be due to the presence of nitrogen groups of aniline moieties in both **PCBA**n and **P-PCBA**n. The aniline groups might involve in electron transfer to fullerene acceptor and hence induce charge imbalance in the BHJ active layer. Similarly, the non-conducting PANI form also may be reducing the charge mobilities across the heterojunctions.⁵⁵

4. Conclusions

In summary, we have successfully synthesized a fullerene-aniline derivative, 3-aminobenzyl-[6,6]-phenyl- C_{61} -butyrate ester (**PCBA**n) and its polymer **P-PCBA**n and investigated their photophysical and morphological properties with a view to understand their potential as acceptor moieties in the PSCs. The optical and electrochemical studies revealed upshifted LUMO levels for **PCBA**n (-3.68 eV, $\Delta E = 0.1$ eV) and **P-PCBA**n (-3.66 eV, $\Delta E = 0.12$ eV) compared to the **PCBM** (-3.78 eV). Moreover, the morphology of **PCBA**n alone in the binary solvent mixture (THF- H_2O) and **P-PCBA**n (in ODCB) were evaluated using AFM and TEM analysis which indicated nanoflake-like aggregates for **PCBA**n and networked

nanostructures for **P-PCBAn**. The solution/solid state fluorescence emission, quenching studies with **P3HT** electron donor indicated **P-PCBAn** as an efficient electron acceptor than **PCBAn**. The morphological analysis of **P3HT: PCBAn** and **P3HT: P-PCBAn** polymer blend film revealed the formation of spherical aggregates and inter-connected networked nanostructures, respectively. The fabrication of BHJ-PSC device with **PCBAn** and **P-PCBAn** in combination with **P3HT** showed relatively higher power conversion efficiency for **P-PCBAn** (PCE = 1.1 %) compared to **PCBAn** (PCE = 0.9%). The increased PCE in case of **P-PCBAn** might be due to the combined effect of bicontinuous interpenetrating network structures and better charge transport properties of **P3HT:P-PCBAn** polymer blend compared to **P3HT:PCBAn**. The polymeric acceptor and rational design strategy used here could open up new opportunities in the PSC device fabrication.

Supplementary Information (SI)

The details of the synthetic procedures, comparison of FT-IR and UV-Visible spectra of **PCBAn** and **P-PCBAn**, MALDI-TOF spectra of **P-PCBAn**, Tables indicating HOMO and LUMO energy levels, aggregation studies, fluorescence quenching and lifetime studies are given in the supplementary information. Supplementary Information is available at www.ias.ac.in/chemsci.

Acknowledgements

The financial support from the Council of Scientific and Industrial Research (CSIR 12 FYP M2D-CSC-0134) and Department of Science and Technology, Government of India (Ramanujan Fellowship Grant RJN-19/2012) are gratefully acknowledged. S.K.V. and R.R. acknowledge University Grant Commission (UGC, Government of India) and CSIR respectively, for Research Fellowship.

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