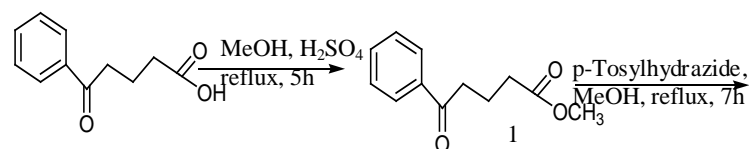


Synthesis, characterization and photovoltaic effect in organic solar cell fabricated with Phenyl-C₆₁-Butyric acid Methyl ester [PCBM] as an electron acceptor layer

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Abstract: Phenyl-C₆₁-Butyric acid Methyl ester [PCBM] synthesized, characterized and studied for photovoltaic properties. Organic solar cell fabricated with the synthesized and also with commercial materials having device structure of ITO/PEDOT:PSS/PCBM:P3HT/LiF/Al. Device characteristics have been measured and compared with commercial materials. The device performance is found comparable to commercial material.

using a 500 MHz spectrometer and calibrated using signals from the solvent and are reported downfield from SiMe₄.



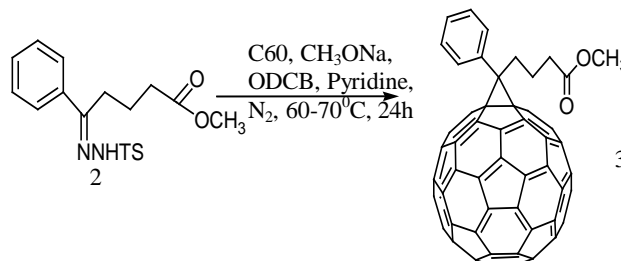
I. INTRODUCTION

Organic solar cells [1] have been attracting much attention around the world in recent years. Organic photovoltaic devices (OPVs) [2] are considered the most promising due to their possibility to create low-cost, flexible [3], extremely light weight solar cells and photo-detectors. Heeger et. al. made the first bulk hetero junction (BHJ) prototype of polymer photovoltaic cells in 1995 [4]. The active layer consists of a blend of electron-donating materials, for example, *p*-type conjugated polymers and electron-accepting (*n*-type) materials. Fullerene derivative, [6, 6]-phenyl C₆₁-butyric acid methyl ester [PCBM] was the most widely used standard reference acceptor material. Several factors are important in further improving the efficiencies of BHJ devices, such as UV-VIS absorption, Highest Occupied Molecular Orbitals (HOMO), Lowest Unoccupied Molecular Orbitals (LUMO), and band gap relations between the donor and the acceptor materials.

In this paper, we report the synthesis and characterization of a C₆₀ derivative, [6, 6]-phenyl C₆₁-butyric acid methyl ester (PCBM) as acceptor material (Scheme 1). Polymer solar cells were made using as prepared and commercial materials in the same batch. The prepared material performance was found slightly better in Organic Photovoltaic devices compared to the commercial material.

II. EXPERIMENT

The chemical structure and synthesis of PCBM are presented in scheme 1. All chemicals, unless otherwise specified, were obtained from Aldrich and used as received. All the solvents were further purified under a nitrogen flow. PCBM was prepared according to the reported synthesis route [5, 6]. ¹H NMR and ¹³C NMR spectra were obtained



Scheme 1: Synthetic routes of [6, 6]-phenyl C₆₁-butyric acid methyl ester [PCBM]

Synthesis of Methyl 4-Benzoylbutyrate[1]: Methyl 4-benzoylbutyrate was prepared from benzoylbutyric acid (6g, 0.0312mol) and methanol (125ml) using 6 drops of H₂SO₄ as catalyst reflux for 5h. After reaction mixture was cooling down, solvent was removed and 50 ml water was added. The reaction product was extracted with dichloromethane to provide an organic layer. The organic layer was separated, dried with MgSO₄ and purified from Column chromatography (eluting solvent 2% acetone in dichloromethane). Solvent was removed to afford the methyl 4-benzoylbutyrate as yellowish oil product (7g). ¹H-NMR, δ (CDCl₃=7.25ppm) 7.95 (m, 2H; ortho HPh), 7.55 (m, 2H), 7.45 (t, 1H), 3.66 (s, 3H, OCH₃), 3.05(t, 2H), 2.44(t, 2H), 2.08 (m, 2H, -CH₂CO₂R). ¹³C-NMR δ (CDCl₃ = 77.00ppm), 199.33, 173.67, 133.03, 128.55, 7.97, 51.54, 37.39, 33.07, 19.28, FTIR (KBr): 3446, 2924, 1734, 1491, 1153 cm⁻¹.

Synthesis of Methyl 4-Benzoylbutyrate p-tosylhydrazone[2]: A mixture of methyl 4-benzoylbutyrate (9g, 0.0436 mol), *p*-toluene sulphonylhydrazide (9.75g, 0.052 mol) and methanol (45ml) was stirred and refluxed for 7h to prepare a reaction mixture. The reaction mixture was allowed to cool at room temperature when crystals started to form. The reaction flask was stored in refrigerator overnight

and the crystalline product was collected by filtration, washed with a small amount of cold MeOH, and dried to afford the tosylhydrazone 8.37g as white crystal.

Synthesis of [6,6]-phenyl C₆₁-butyric acid ester[3]:

Methyl 4-benzoylbutyric acid ester *p*-tosylhydrazone (2g, 5.32 mmol) was dissolved in 40ml of dry pyridine in dry three-necked flask under N₂ flow. Then sodium methylate (0.312g, 5.76mmol) was added and the mixture was stirred for 30 min at room temperature. A solution of C₆₀ (1.92g, 2.66mmol) in dry 1, 2 dichlorobenzene (130ml) was added, and then stirred at 70°C for 22h. The reaction mixture transferred to the one neck R. B. flask and concentrated by distillation. The concentrated solution poured on the silica gel/toluene column (40X10 cm), pre eluted with 200ml of chlorobenzene and then with toluene. A fraction containing unreacted C₆₀ was collected first. After that [6, 6]-phenyl C₆₁-butyric acid ester [PCBM] was collected and solvent removed to afford a dark brown solid. 1, 2-Dichlorobenzene added to the brown solid and the resulting mixture heated to reflux for 7h under N₂. The solvent was removed in vacuum and resulting residue dissolved in dichloromethane (DCM) (25ml). Methanol was added and the resulting precipitate was collected by filtration and dried in vacuum to afford PCBM (1.2g). ¹HNMR (CDCl₃): 7.97 (d, 2H; o-H arom), 7.58 (m, 2H; m-H arom), 7.17 (m, 1H; *p*-H arom), 3.73(s, 3H; OCH₃), 2.16 (t, 2H; CH₂CO₂Me), 1.56 (m, 2H; Ph(C₆₀)CH₂), 1.44 (m, 2H; CH₂CH₂CO₂Me). ¹³CNMR (CDCl₃) = 192.50 ppm): 173.47(CO₂Me), 147.45, 146.53, 145.25, 144.88, 144.59, 144.33, 144.05, 143.85, 143.75, 143.66, 143.23, 142.82, 142.66, 142.23, 141.98, 141.41, 141.12, 140.56, 139.88, 139.79, 138.89, 138.27, 137.93, 136.59, 135.14, 130.86, 128.77(Ph C_{2,3}), 125.39(Ph C_{2,3}), 65.94(PhC), 51.74 (OCH₃), 35.43(PhCC), 33.99(CCO₂), 19.93(CCCO₂). FTIR (KBr): 3446, 2924, 1734, 1491, 1429, 1247, 1153, 1076, 1024, 838, 754, 733, 698, 643, 583, 572, 572, 549, 525 (s) cm⁻¹.

III. RESULTS

The absorption spectra of PCBM (Fig1) are recorded

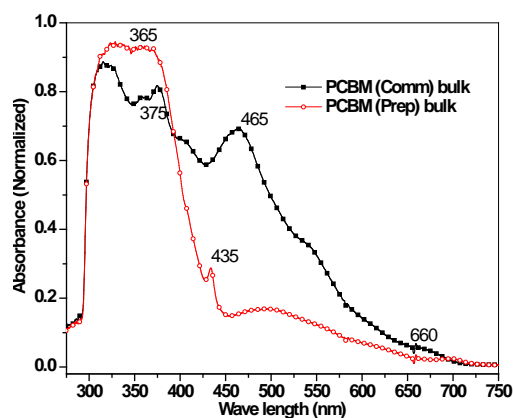


Fig. 1: Absorption spectra of [6,6]-phenyl C₆₁-butyric acid methyl ester [PCBM]

in solution using 1, 2 dichlorobenzene as a solvent and the peak maxima are observed at 365nm & 435nm and 375nm & 465nm for as-prepared PCBM and commercial PCBM respectively. The optical band gap calculated from absorption edge of as-prepared PCBM and commercial PCBM is 1.69eV and 1.74eV respectively. It is concluded that there is no dramatic change in the absorption spectra of both the compounds.

Photoluminescence [PL] spectrum of PCBM recorded in solid state using 325nm Xe laser excitation source is shown in Fig.2. The spectra has dominated PL peak centered at 412nm in both the cases and Full Width at Half Maxima (FWHM) are ~135nm in commercial and 147nm in as-prepared PCBM. There is a significant shift of the PL intensity in as-prepared material with comparison to commercial material.

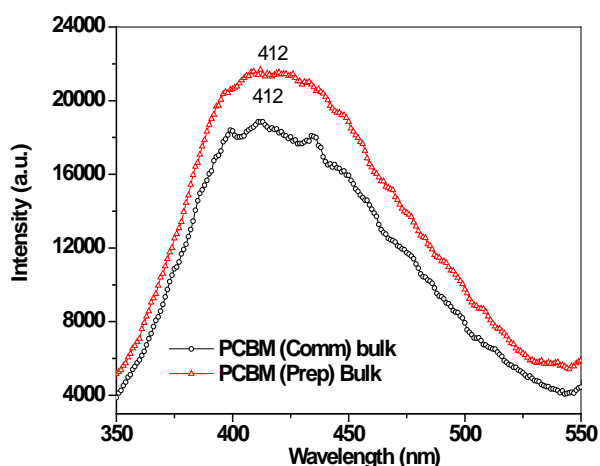


Figure2: Photoluminescence [PL] spectrum [6, 6]-phenyl C₆₁-butyric acid methyl ester [PCBM]

The electrochemical measurements of the PCBM molecules were performed in an electrolyte consisting of 0.1mol/L tetrabutylammonium hexafluorophosphate (TBAPF₆) dissolved in 1, 2-dichlorobenzene solution. In each case, a platinum disc was used as the working electrode, platinum wire was used as a counter electrode, and a saturated Ag/AgCl₃ electrode was used as a reference electrode. The redox behavior of PCBM was determined by cyclic voltammetry (CV) measured under identical conditions. The cyclic voltammograms are shown in Fig.3.

Cyclic Voltammograms showed four reversible reduction peaks in both the cases. The PCBM (-0.54 V) showed a clearly diminished electron affinity in both the cases. The LUMO value is calculated from the onset reduction potential and HOMO value is calculated from the addition of band gap to the LUMO value of the both material. The HOMO and LUMO value are 6.0eV & 4.26eV and 5.95eV and 4.26eV for commercial and as-prepared PCBM respectively.

TABLE1: Comparison of properties of commercial and as-prepared PCBM.

Compound	Absorption (nm)	PL (nm)	HOMO (eV)	LUMO (eV)	V _{oc} (V)	Band gap (eV)	I _{sc} (mA/cm ²)	FF
As Prepared PCBM	365, 435	412	5.95	4.26	0.54	1.69	4.35	54%
Commercial PCBM	375, 465	412	6.0	4.26	0.37	1.74	4.77	27%

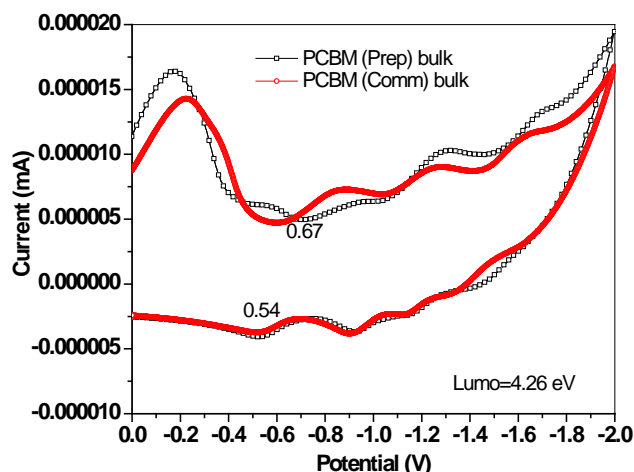


Fig. 3 Cyclic Voltammetric [6, 6]-phenyl C₆₁-butyric acid ester [PCBM]

The solar cells of structure ITO/PEDOT: PSS/P3HT: PCBM/LiF/Al was fabricated using commercial and as-prepared PCBM. The P3HT and PCBM were mixed in 1:1 ratio and spin coated to make bulk hetero-junction. Figure 4 shows a comparison of the Current –Voltage (I-V) curves of the commercial and as-prepared PCBM based BHJ solar cells. The important characterizing parameters, Open Circuit Voltage (V_{oc}), Short Circuit Current (I_{sc}) and Fill Factor (FF) in case of commercial and as-prepared materials devices are given Table 1. The device performance of

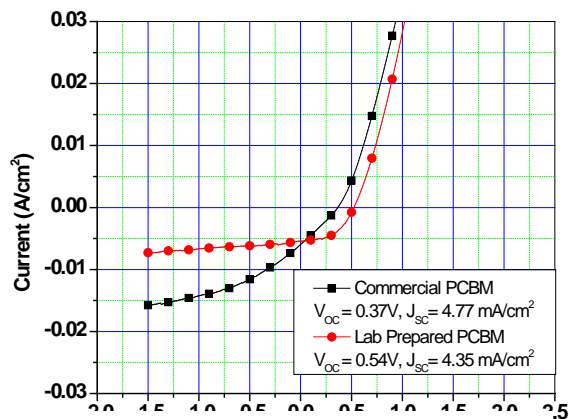


Fig. 4: I-V graph of the organic PV device of PCBM: P3HT active layer

as-prepared PCBM (V_{oc} = 0.54), Fill factor 54%) is better in comparison to commercial PCBM (Fill factor 27%). However, Short circuit current is better in devices made using commercial material.

IV. CONCLUSION

PCBM is indigenously synthesized in lab using reported synthesis route [5,6]. Polymer solar cells were made from as-prepared and commercial PCBM materials. The devices made out of as-prepared material showed better V_{oc} and Fill Factor. Further, investigation is under way to find out the cause.

V. ACKNOWLEDGEMENT

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