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1-(3-Methoxycarbonyl)propyl-2-selenyl-[6,6]-methanofullerene as a n-Type Material for Organic Solar Cells

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ABSTRACT

Demand for green and renewable energy is stimulating research into future materials for energy production. Thin films of materials possessing both electron accepting and donating functions play a unique role in solar energy technology because of their light weight, flexibility, and economical, low-temperature, and large-area fabrication. A [60]fullerene derivative, [6,6]-2-selenyl-C_{61}-butyric acid methyl ester (SeCBM), has been synthesized in three steps, namely through Friedel–Crafts acylation of selenophene, hydrazone formation and Bamford-Steven reaction. Organic photovoltaic device incorporating SeCBM and the conducting polymer P3HT exhibited an average power conversion efficiency of 3.26% and a champion efficiency as high as 3.81% under AM 1.5G irradiation.

1. Introduction

Demand for green and renewable energy is stimulating research into future materials for energy production. Solar energy technology is arguably the cleanest approach toward power generation. Thin films of materials possessing both electron accepting and donating functions play a unique role in solar energy technology because of their light weight, flexibility, and economical, low-temperature, and large-area fabrication. Because fullerene derivatives are good electron acceptors [1,2], they have become useful materials in thin film organic solar cells [3–18]. In particular, the commercialized fullerene derivative **PCBM** ([6,6]-phenyl-C_{61}-butyric acid methyl ester; [6,6]-**3a**) is at present the most often used n-type material in studies of organic photovoltaics (OPVs) [19]. Improved power conversion efficiency generally used **PCBM** [20,21,8,22–24] or non-methanofullerenes [25,26] as n-type materials, or alternatively utilized other newly designed polymers [27–33]. Several structurally similar fullerenes also exhibit remarkable photoconversion efficiencies when blended with conductive polymers poly(3-hexylthiophene) (**P3HT**); for example, **ThCBM** ([6,6]-2-thienyl-C_{61}-butyric acid methyl ester; [6,6]-**3b**) displays a value of power conversion efficiency (PCE) comparable to that of [6,6]-**3a** (ca. 4.0%) [34–36]. We thought that incorporation of selenyl moiety in the device may improve photovoltaic performance. The LUMO energy levels of the fullerenes can be slightly adjusted through homo-conjugation in the methanofullerenes [37]. Although synthetic methods have been available for preparation of **PCBM** and **ThCBM**, transfer of the approaches to the synthesis of **SeCBM** is limited by the poor reactivity of selenophene for functionalization. In this paper, we present our studies in developing novel derivative of **SeCBM** ([6,6]-2-selenyl-C_{61}-butyric acid methyl ester; [6,6]-**3c**) possessing selenyl moiety and exploring its electrochemical properties and photovoltaic performance incorporated into an organic solar cell device.

2. Experimental

2.1. Material and methods

2.1.1. BF_3-mediated synthesis of 5-oxo-5-selenophen-2-yl-pentanoic acid methyl ester (**1c**)

To a sealed tube containing selenophene (150 mg, 1.14 mmol), methyl 5-chloro-5-oxovalerate (224 mg, 1.36 mmol) and 1.2 equiv of BF_3 etherate in anhydrous 1,2-dichloroethane was heated at 84 °C for 5 h under argon. The reaction mixtures were cooled and poured onto sat. $NaHCO_{3(aq)}$ and extracted with dichloromethane. The extract was dried with Na_2SO_4, and subjected to SiO_2 chromatography to give 72% of **1c** (251 mg) after dryness. R_f: 0.33

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Table 1
Friedel–Crafts acylations of selenophene and thiophene with methyl 5-chloro-5-oxovalerate.

Entry	Reactant[a]	Reagent[a]	Solvent	Temp (°C)	*t* (h)	Yield (%)
1	Selenophene	$AlCl_3$	DCM	rt	5	48
2	Selenophene	BF_3	DCM	rt	18	60
3	Selenophene	BF_3	DCE	84	6	72
4	Thiophene	$AlCl_3$	DCE	rt	5	45
5	Thiophene	BF_3	DCM	rt	5	Trace
6	Thiophene	BF_3	DCE	84	6	53

[a] 1 equiv with respective to that of methyl 5-chloro-5-oxovalerate.

(CH_2Cl_2). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.08 (m, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 3.00 (t, *J* = 7.2 Hz, 2H), 3.68 (s, 3H), 7.37–7.41 (m, 1H), 7.94 (d, *J* = 3.1 Hz, 1H), 8.37 (d, *J* = 5.1 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 19.6, 32.8, 37.2, 51.3, 130.6, 134.1, 139.7, 150.8, 173.3, 193.2. EI-Ms *m*/*z*: calcd for $C_{10}H_{12}O_3Se$ (M^+): 260.0; found: 260.0 (M^+), 158.9 (100%), 156.9 (48%). HRMS (FAB): calcd for $C_{10}H_{12}O_3Se$ (M^+): 259.9952; found: 259.9954. FT-IR ν (cm^{-1}) 713, 1149, 1175, 1211, 1425, 1529, 1656, 1734, 2951, 3097.

*2.1.2. Synthesis of 5-Selenophen-2-yl-5-(toluene-4-sulfonylimino)-pentanoic acid methyl ester (**2c**)*

A mixture of **1c** (146 mg, 0.560 mmol), *p*-toluenesulfonyl hydrazide (127 mg, 0.680 mmol), and MeOH (1 mL) was refluxed for 3.5 h under argon. To this mixture was added *p*-toluenesulfonyl hydrazide (127 mg, 0.680 mmol) again. After 24 h, the mixture was cooled to room temperature and added water. The product was collected by filtration, washed with water, and dried in dichloromethane by sodium sulfate to yield 191 mg (79%) of tosylhydrazone **2c** as yellow powders. m.p. 121–122 °C. R_f: 0.17 (EA:Hexanes = 1:1). ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.73 (m, 2H), 2.32 (t, *J* = 3.0 Hz, 2H), 2.41 (s, 3H), 2.61 (t, *J* = 4.0 Hz, 2H), 3.77 (s, 3H), 7.21 (m, 1H), 7.29 (m, 2H), 7.34 (m, 1H), 7.89 (m, 2H), 7.93 (m, 1H), 9.12 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 21.1, 21.5, 26.1, 32.0, 52.3, 128.0, 128.5, 129.4, 129.7, 133.0, 135.5, 143.8, 148.4, 151.7, 174.7. EI-Ms *m*/*z*: calcd for $C_{17}H_{20}N_2O_4SSe$ (M^+): 428.0; found: 428.1 (M^+), 171.0 (100%), 91.1 (72%). HRMS (EI): calcd for $C_{17}H_{20}N_2O_4SSe$ (M^+): 428.0309; found: 428.0303. FT-IR ν (cm^{-1}) 563, 668, 707, 1168, 1227, 1335, 1350, 1438, 1715, 1734, 2925, 2954, 3202.

*2.2. Synthesis of compound **SeCBM** ([6,6]-**3c**)*

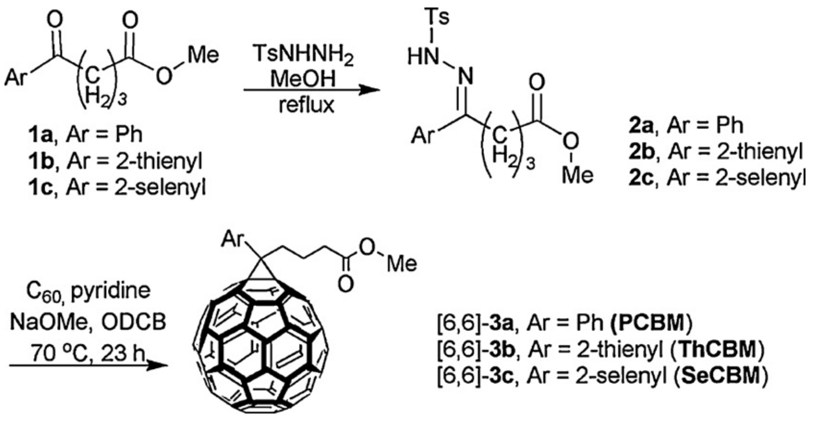
Compound **2c** (43 mg, 0.10 mmol) was dissolved in 1.5 mL of anhydrous pyridine in a dried two-necked flask provided with argon inlet and a magnetic stirring bar. Then, NaOMe (11 mg, 0.20 mmol) was added, and the mixture was stirred for 30 min. A solution of 72 mg (0.10 mmol) of C_{60} in 8 mL of anhydrous 1,2-dichlorobenzene was added, and the homogeneous reaction mixture was stirred at 70 °C for 23 h. Next, to this solution was added 1 equiv of NaOMe per hour until 5 equiv of NaOMe was added. The course of the reaction was followed by HPLC and TLC (SiO_2/toluene) analyses. The mixture was added a small amount of hexanes to reduce polarity and then the mixtures were subjected to flash chromatography. The starting material C_{60} (41 mg, 57%) was first recovered with toluene as initial eluent. Next, compound [5,6]-**3c**/[6,6]-**3c**, with ratio of 13:87, was isolated as brown solids (22 mg, 23%; 53% based on converted C_{60}). The whole mixture was transformed to [6,6]-**3c** by irradiation with a halogen lamp. R_f: 0.48 (toluene). The scale of this reaction can be conducted with a gram-scale of C_{60} (1.008 g) in 110 mL of 1,2-dichlorobenzene and this provided 287 mg of **SeCBM** ([6,6]-**3c**) in 20% yield (50% based on converted C_{60}; with 583 mg (54%) recovered C_{60}). Spectral data for [6,6]-**3c** follow. ^{1}H NMR (700 MHz, $CDCl_3$): δ 2.26 (m, 2H), 2.59 (t, *J* = 7.0 Hz, 2H), 2.96 (m, 2H), 3.7 (s, 3H), 7.36 (dd, *J* = 4.2, 6.2 Hz, 1H), 7.66 (d, *J* = 4.2 Hz, 1H), 8.17 (d, *J* = 6.2 Hz, 1H). ^{13}C NMR (175 MHz, $CDCl_3$): δ 22.51, 33.7, 34.39, 47.87, 51.72, 80.44, 128.54, 132.15, 134.71, 138.14, 138.32, 140.77, 140.97, 142.12, 142.15, 142.18, 142.93, 142.96, 143.03, 143.05, 143.07, 143.1, 143.12, 143.8, 143.83, 144.19, 144.51, 144.61, 144.67, 144.72, 144.74, 144.84, 145.08, 145.15, 145.21, 145.24, 145.26, 145.69, 145.91, 147.49, 148.28, 173.49. UV–Vis λ_{max} (ε) ($CHCl_3$, 4.88×10^{-5} M): 229 (1.21×10^5), 260 (1.56×10^5), 327 (4.68×10^4), 432 (3.49×10^3), 493 (2.26×10^3). FAB-MS *m*/*z*: calcd for $C_{70}H_{12}O_2Se$ (M^+): 964; found: 964. HRMS (FAB): calcd for $C_{70}H_{13}O_2Se$ (M^++H^+): 965.0081; found: 965.0083. FT-IR ν (cm^{-1}) 526, 575, 754, 1172, 1188, 1213, 1250, 1430, 1456, 1734, 2946, 3018.

2.4 The device fabrication procedure was identical to that used previously to obtain devices based on **P3HT** and [6,6]-**3a** [38,39].

3. Results and discussion

3.1. Synthesis and characterization

We prepared **SeCBM** starting with Friedel–Crafts acylation of selenophene with methyl 5-chloro-5-oxovalerate, mediated by Lewis acids (Table 1). Initially, we used $AlCl_3$ to mediate the acylation in anhydrous CH_2Cl_2 at room temperature, but obtained only 40–50% yields of **1c** (Table 1, entry 1) [40]. When we switched to less acidic $BF_3{\cdot}OEt_2$ as the Lewis acid, we obtained higher acylating yields: 60% at room temperature and 72% at 84 °C (entries 2 and 3, respectively); the latter providing **1c** in a straightforward manner and large quantity in a single step. Although this acylation approach was a good alternative for the large-scale synthesis of **1c**, the corresponding acylations of thiophene mediated by $AlCl_3$



Scheme 1. Syntheses of [6,6]-**3a**–**c**.

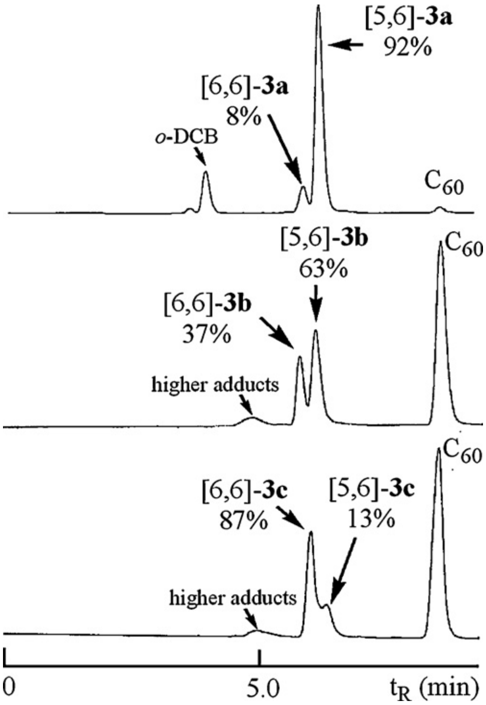


Fig. 1. HPLC chromatograms displaying the ratios of [5,6] and [6,6] isomers obtained at reaction times of 22 h during the syntheses of **PCBM** ([6,6]-**3a**), **ThCBM** ([6,6]-**3b**), and **SeCBM** ([6,6]-**3c**) (Buckyprep column; flow rate, 1 mL h^{-1}; toluene; 30 °C; detection wavelength = 326 nm).

or BF_3 provided only moderate yields (40–53%) of **1b** (entries 4–6). The next reaction of **1c** with *p*-tolylsulfonylhydrazine gave **2c** in good yield (>90%).

With precursor **2c** available in a bulk quantity, we performed the Bamford–Steven reaction in the dark to prepare **SeCBM** ([6,6]-**3c**, Scheme 1). Under conditions similar to those used to prepare [6,6]-**3a** and [6,6]-**3b**, we found that the addition of larger amounts of base (pyridine and NaOMe; >5 equiv added sequentially) was necessary to achieve comparable yields (ca. 40%). In average, we achieved 23% isolated yields of [6,6]-**3c** (53% yields based on converted C_{60}). This was attributed to the fact that precursor **2c** incorporating selenyl functionality was relatively less reactive as compared to those for preparing [6,6]-**3a** and [6,6]-**3b**.

It was interesting to note that the [5,6]- and [6,6]-isomeric ratios are dramatically different while preparing [6,6]-**3a**, [6,6]-**3b** and [6,6]-**3b**, respectively. From HPLC analytical data obtained at 22 h of the reactions, we found a 92:8 mixture of [5,6]-**3a** and [6,6]-**3a**, and a 63:37 mixture of [5,6]-**3b** and [6,6]-**3b**; in contrast, an excess of the [6,6]-**3c** product, with a [5,6]-**3c**/[6,6]-**3c** ratio of 13:87 was observed (Fig. 1). Whereas the isolated mixtures of [5,6]-**3a**/[6,6]-**3a** and [5,6]-**3b**/[6,6]-**3b** were transformed to their [6,6]-**3a** and [6,6]-**3b** adducts, respectively, upon irradiation of their toluene solutions with a halogen lamp at a distance of 25 cm for 3 h, the **3c**-[5,6]/**3c**-[6,6] mixture was fully transformed to the [6,6]-**3c** isomer under much milder conditions: by mere exposure to ambient light or by a halogen lamp in few minutes [41]. Transformation of the [5,6]-isomer to [6,6]-isomer is necessary because [5,6]-isomer is a fully π-conjugated fulleroid that exhibits lower LUMO energy levels and thus renders it to form lower open-circuit voltage (V_{oc}) with P3HT in the device. For examples, the first reduction s (with reference to ferrocene/ferrocenium) of isomeric mixtures consisting of [5,6]-**3a**/[6,6]-**3a** (molar ratio = 92:8) is about 40 mV more anodic shift to that of pure [6,6]-**3a**. It is noteworthy that commercial **PCBM** comprises only the [6,6]-isomer.

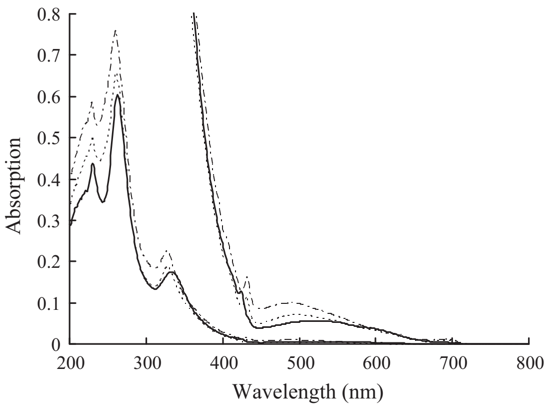


Fig. 2. UV–Vis spectra of [6,6]-**3a** (—, 5.1 × 10^{-5} M), [6,6]-**3b** (- - -, 5.1 × 10^{-5} M), and [6,6]-**3c** (– – –, 4.9 × 10^{-5} M) in $CHCl_3$.

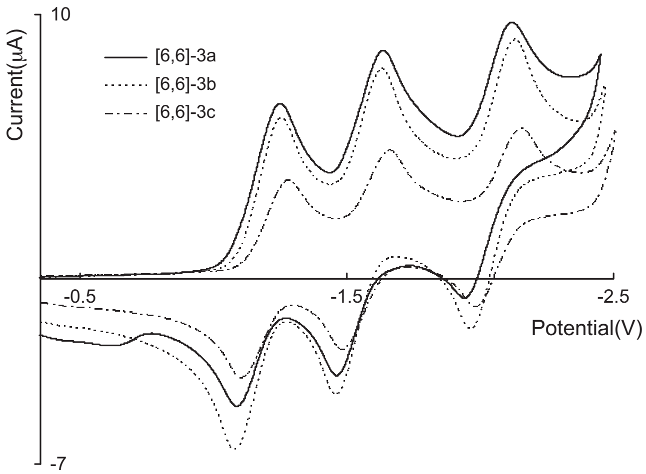


Fig. 3. CV traces of [6,6]-**3a** (—, 0.50 mM), [6,6]-**3b** (- - -, 0.45 mM), and [6,6]-**3c** (– – –, 0.50 mM) in anhydrous *o*-DCB. Scanning rate: 50 mV s^{-1}.

We characterized **SeCBM** ([6,6]-**3c**) using spectroscopic methods. Its molecular ion appeared at *m*/*z* 965.0083 (HR-FAB$^+$; calcd for $C_{70}H_{13}O_2Se$, 965.0081 [M+H]$^+$). The ^{13}C NMR spectrum supported the structure of a [6,6] isomeric compound, with the signal for the C(61) carbon appearing at 47.9 ppm and the only sp^3-hybridized carbon atom of the fullerene appearing at 80.4 ppm. The IR spectrum of [6,6]-**3c** revealed the presence of an ester moiety at 1734 cm^{-1}. UV–Vis spectra of the three compounds [6,6]-**3a**–**c** revealed interesting features. Typical absorptions of fullerene mono-adducts appeared at 430 nm for [6,6]-**3b** and [6,6]-**3c**, whereas the signal appeared at 424 nm for [6,6]-**3a**. The broad humps spanning from 440 to 660 nm were hypsochromically shifted for [6,6]-**3b** and [6,6]-**3c**, relative to that of [6,6]-**3a**. The small, narrower humps at 660–720 nm were even more hypsochromically shifted for [6,6]-**3b** and [6,6]-**3c**. Notably, both

Table 2
Half-wave reduction potentials (V)[a] of [6,6]-**3a**–**c**.

Compound	E^1	E^2	E^3
C_{60}[b]	−1.13	−1.50	−1.95
[6,6]-**3a**	−1.206	−1.581	−2.076
[6,6]-**3b**	−1.194	−1.572	−2.066
[6,6]-**3c**	−1.190	−1.569	−2.066

[a] Versus ferrocene/ferrocenium. Conditions: ca. 0.50 mM C_{60}, [6,6]-**3a**, [6,6]-**3b**, [6,6]-**3c** and 0.050 mM Bu_4NPF_6 in anhydrous *o*-DCB; reference electrode: Ag/0.01 M $AgNO_3$ and 0.050 mM $(n\text{-Bu})_4NClO_4$ in anhydrous MeCN; working electrode: glassy carbon; auxiliary electrode: Pt; scanning rate: 50 mV s^{-1}.

[b] See Ref. [42].

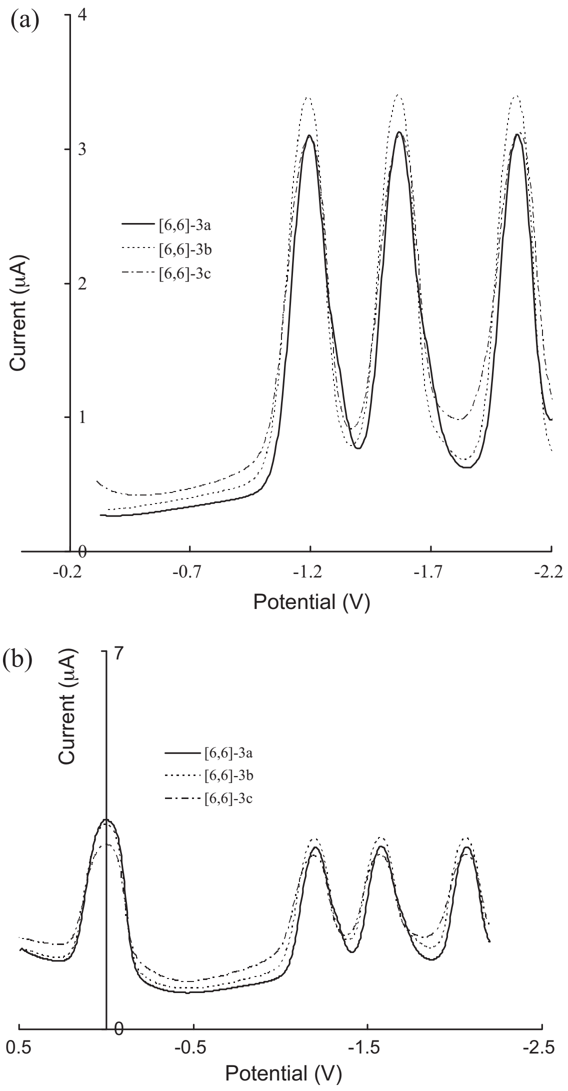


Fig. 4. (a) DPV and (b) OSWV traces of [6,6]-**3a** (—), [6,6]-**3b** (---), and [6,6]-**3c** (–––). Square amplitude: 25 mV; frequency: 15 Hz; step *E*: 4 mV.

[6,6]-**3b** and [6,6]-**3c** exhibited slightly larger molar absorptivities than [6,6]-**3a** between 420 and 550 nm (Fig. 2).

3.2. Redox properties

Next, we used cyclic voltammetry (CV), differential pulse voltammetry (DPV) and Osteryoung square wave voltammetry (OSWV) to examine the redox properties of [6,6]-**3a**–**c** and revealed any subtle changes in their electronic properties. Table 2 lists the half-wave reduction potentials of [6,6]-**3a**–**c** relative to ferrocene/ferrocenium. Fig. 3 displays cyclic voltammograms of [6,6]-**3a**–**c** measured at scanning rate of 50 mV s^{-1}. The first reductive potentials of [6,6]-**3a** is ca. 12 mV more negative than that of [6,6]-**3b**. The selenyl fullerene [6,6]-**3c** displayed its first half-wave reduction potential at −1.190 V; this value is ca. 60 mV more negative (cathodic shift) than that of C_{60} and only 4 mV less negative (anodic shift) than that of [6,6]-**3b**, respectively. The second reduction of [6,6]-**3c** occurred at −1.569 V, which is 12 and 3 mV less negative than those of [6,6]-**3a** and [6,6]-**3b** respectively.

Since the half-wave reduction potential differences are minute, we used DPV (Fig. 4a) and OSWV (Fig. 4b) traces to confirm the relative orders of these reduction potentials of [6,6]-**3a**–**c**. Their first reduction potentials are −1.196, −1.188 and −1.196 V by DPV and −1.202, −1.194 and −1.188 V by OSWV, respectively. According to CV, DPV and OSWV analyses, [6,6]-**3a** remains to be the one having the highest LUMO energy level (referred to Fc/Fc$^+$). But the LUMO levels of [6,6]-**3a** and [6,6]-**3b** are too close to be distinguished; their relatives orders could not be determined accurately. The electrochemical study suggests that [6,6]-**3a** possesses the highest LUMO energy level among all three of the [6,6]-isomers [6,6]-**3a**–**c**. Because of the open circuit voltage (V_{oc}) is determined by the difference between the HOMO energy level of the polymers and the LUMO energy level of fullerenes. The higher LUMO levels (with more negative reduction potential) of the fullerene derivatives correspond to higher values of V_{oc} in the fabricated devices [27,43,44]. Thus, we would expect that devices incorporating [6,6]-**3a** remains to exhibit the largest open-circuit voltage (V_{oc}) among the studied compounds.

Table 3
Physical data of devices incorporating [6,6]-**3a**–**c** and **P3HT** (1:1, w/w).

Compound	V_{oc}	J_{sc}	PCE	FF
[6,6]-**3a**	0.59	9.00	3.54	66%
[6,6]-**3b**	0.58	9.18	3.02	57%
[6,6]-**3c**	0.55	8.93	3.26	66%

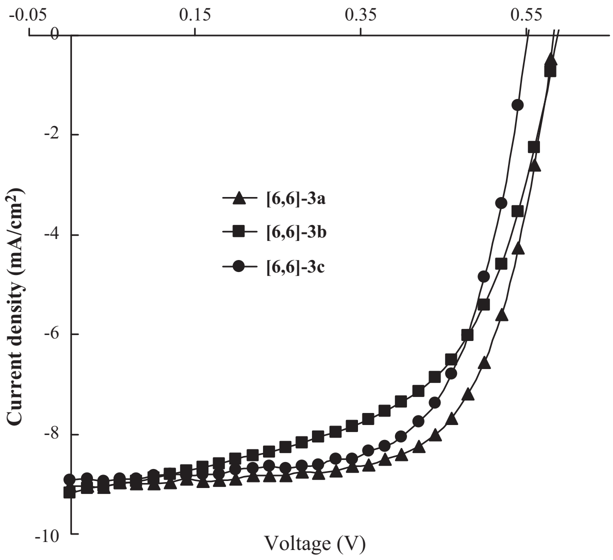


Fig. 5. *J*–*V* curves of solar cells incorporating the fullerene derivatives [6,6]-**3a**, [6,6]-**3a** and [6,6]-**3c** with **P3HT**.

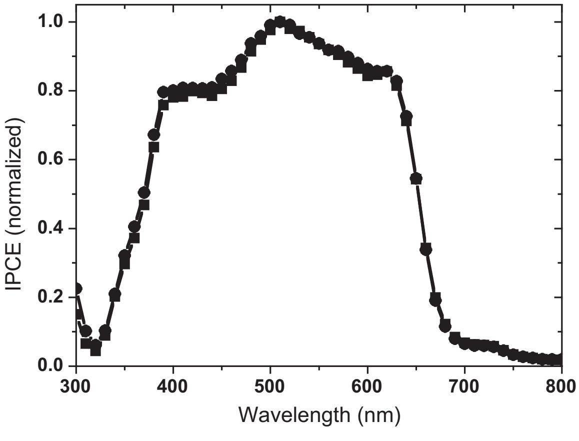


Fig. 6. IPCE spectra of thin film consisting of [6,6]-**3b/P3HT** (■) and [6,6]-**3c/P3HT** (●).

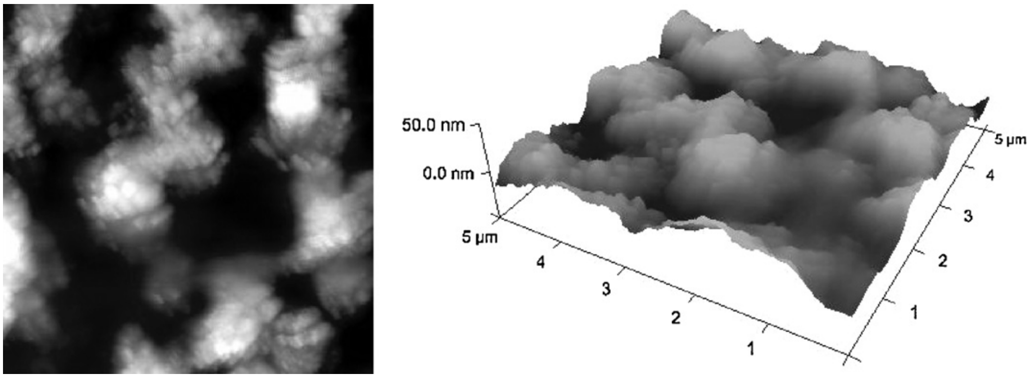


Fig. 7. Atomic force microscopy (AFM) image of thin film with [6,6]-**3c/P3HT** as an active layer.

3.3. Photovoltaic performance studies

With a large amount of **SeCBM** in hand, we fabricated photovoltaic devices incorporating [6,6]-**3a**–**c** and **P3HT** (1:1, w/w) respectively. We fabricated photovoltaic cells by spin-coating the blends from *o*-DCB solution. The OPVs, with layered configuration of glass/ITO/PEDOT:PSS/P3HT:fullerenes (15 mg/mL 1:1, w/w)/Ca/Al, were fabricated using known methods [38,39]. Table 3 summarizes the device performances of the solar cells incorporating [6,6]-**3a**–**c** and **P3HT** (see Fig. 5 for *J*–*V* plots). The average power conversion efficiency (PCE) of 3.54% for the [6,6]-**3a**/**P3HT**-based device is comparable to reported values [38]; the PCE for the [6,6]-**3b**/**P3HT**-based device was lower (3.02%), presumably because of the poorer solubility of [6,6]-**3b**. However, the device incorporating **SeCBM** ([6,6]-**3c**) exhibited a slightly higher PCE (3.26%) than that of the device containing [6,6]-**3b**, featuring V_{oc}, J_{sc} and FF of 0.55, 8.93, and 66% respectively. The best PCE was recorded at 3.81% for [6,6]-**3c** and **P3HT** (1:1, w/w)! It is noteworthy that device incorporating [6,6]-**3c/P3HT** displays slightly higher average PCE (3.26%) as compared to that incorporating [6,6]-**3b/P3HT** (3.02%) despite the LUMO energy level of [6,6]-**3b** is slightly higher, which was likely attributed to the poorer solubility of [6,6]-**3b**. This difference can also be interpreted from their normalized incident photon-to-current conversion efficiency (IPCE) as shown in Fig. 6. In this measurement, the higher PCE for [6,6]-**3c/P3HT** film is confirmed by the integration from 300 to 800 nm – the overall integration for [6,6]-**3c/P3HT** is slightly higher than that of [6,6]-**3b/P3HT**. In the morphology study, the surface of the photoactive film consisting of [6,6]-**3c/P3HT** possesses homogeneous morphologies with slightly higher roughness (rms roughness $\sigma = 11.1$ nm), which is verified by atomic force microscopy (Fig. 7). It is interesting to observe that the morphology is quite similar to that displayed by [6,6]-**3b/P3HT** film. [36]

The device performance of [6,6]-**3c/P3HT** up to 3.81% indicates that [6,6]-**3c** could be served as another n-type candidate materials for application in OPVs. One may argues that the starting materials – selenophene – used for synthesis of [6,6]-**3c** is costly and environmental unfriendly and this study will not be helpful for green energy pursuit. However, selenophene can be prepared from dialkyl selenides or selenium powder with acetylene in practical syntheses; thus, its source is not an issue. **SeCBM**, incorporating a selenium atom in the molecule, is not toxic material because it is nonvolatile with decomposition temperature greater than 360 °C under vacuum. [45,46]

4. Conclusions

The selenyl-fullerene [6,6]-**3c** can be obtained in bulk quantities through sequential $BF_3 \cdot OEt_2$-mediated acylation of selenophene, hydrazone formation, and Bamford–Steven reaction. A device incorporating [6,6]-**3c** and **P3HT** exhibited an average PCE of 3.26% and champion efficiency at 3.81%, comparable with those of corresponding devices based on **PCBM** and **ThCBM**. Our results show than the average device performance incorporating **SeCBM** supersedes that made with **ThCBM** in the active layer.

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