Synthesis and properties of novel methanofullerenes having ethylthienyl and/or *n*-pentyl group for photovoltaic cells

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A B S T R A C T

Novel methanofullerenes **3** having ethylthienyl and/or *n*-pentyl groups were designed and synthesized for the purpose of developing new acceptors for an organic photovoltaic cell with higher performance than that of the [6,6]-phenyl-C_{61}-butylic acid methyl ester (PCBM) used as the standard acceptor. The electronic absorption spectra and cyclic voltammetry (CV) of **3**, PCBM, and [6,6]-(thiophene-2-yl)-C_{61}-butylic acid methyl ester (ThCBM) were measured to estimate solubility and reduction potentials as characteristics of n-type semiconductor for organic photovoltaic devices. The CV measurements revealed reversible reduction waves for all of the methanofullerenes and the first reduction potentials of the *n*-pentyl-substituted 1-(5-ethylthiophene-2-yl)-[6,6]-methanofullerene[60] (**3b**) and 1-phenyl-[6,6]-methanofullerene[60] (**3c**) were negatively shifted compared to those of the corresponding terminal methyl ester-substituted homologues (**3a** and PCBM). The performances of photovoltaic devices consisting of **3b** and **3c** were slightly higher than those of PCBM.

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1. Introduction

Ever since silicon-based solar cells were first manufactured for practical use, there has been considerable expectation that photovoltaic system would provide a solution to the energy crisis and the environmental problems related to global warming. Although silicon-based solar cells, due to their relatively high efficiency for energy conversion, have maintained their unrivaled position as energy converting devices for a long time,[1] their poor cost performance and the unstable supply of silicon have prevented the extensive prevalence of these systems. In spite of their lower energy conversion, organic photovoltaic cells are attractive as a promising alternative to silicon-based devices because of their low weight, flexibility, and anticipated low manufacturing costs. In particular, since Sariciftci et al. reported that a conversion efficiency of 2.5% could be achieved using a polymer solar cell based on a bulk heterojunction of [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) and poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV),[2] the polymer/methanofullerene photovoltaic system has attracted a great deal of attention as one of the incoming photovoltaic systems after silicon-based solar cells. Since then, poly(3-hexylthiophene) (P3HT) has been used as p-type semiconductor instead of PPV derivatives because of its high mobility. Subsequently, PCBM and P3HT were frequently used as standard n-type and p-type organic semiconductors, respectively, for polymer/methanofullerene photovoltaics,[3] and the performance of these devices has steadily advanced to a conversion efficiency of greater than 4%,[4] owing to the accumulation of device preparation know-how, mainly with respect to morphological control of the active layers in the deposition, spin-coating, and annealing process.

In order to achieve drastic improvements in device performance, the exploration of more appropriate materials is also an important approach, and several types of polymers have been considered as P3HT and MDMO-PPV alternatives.[5] In contrast, alternatives to PCBM in the polymer/methanofullerene system have been very limited, except for a few analogues of PCBM, and there is no information about the optimum molecular structure of acceptors to maximize the performance.[6]
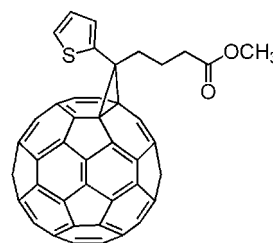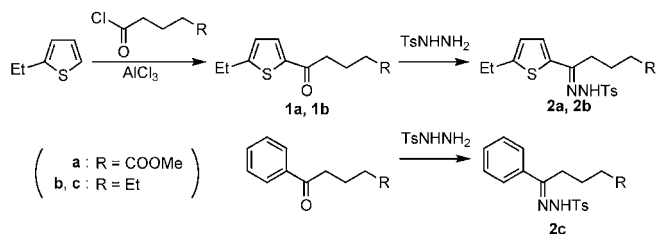

ThCBM

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Recently, Hummelen et al. reported a device fabricated with a thienyl analogue, ThCBM,[7] for the purpose of improving the miscibility with P3HT. However, there was no clear explanation of the advantages of ThCBM over PCBM. In our previous study, we prepared novel PCBM analogues having various types of thienyl groups and investigated their structural effect on the solubilities and morphologies of their mixtures with P3HT.[8] The morphology of the bulk hetero films of the obtained methanofullerenes was found to be different from that of PCBM and the aggregation of P3HT was restricted by the large volume of the substituents of meth-anofullerenes. An improvement in solubility by adding an ester group was also shown.

In this study, novel analogues of PCBM with the phenyl group replaced by a 2-(5-ethylthienyl) group, or the 3-(methoxycarbonyl) propyl group by a *n*-pentyl group, were designed and synthesized, for the purpose of developing new acceptors on P3HT/meth-anofullerene devices having much higher performance than a P3HT/PCBM system and acquiring a guideline for designing optimum molecular structures for them. The 2-(5-ethylthienyl) group was selected instead of thienyl group because of stabilization of the oxidizable α-proton of thiophene by alkylation. We investigated the basic properties, such as the electronic absorption spectra, solubility of these novel methanofullerenes, and perfor-mance of photovoltaic devices that consisted of P3HT and these methanofullerenes.
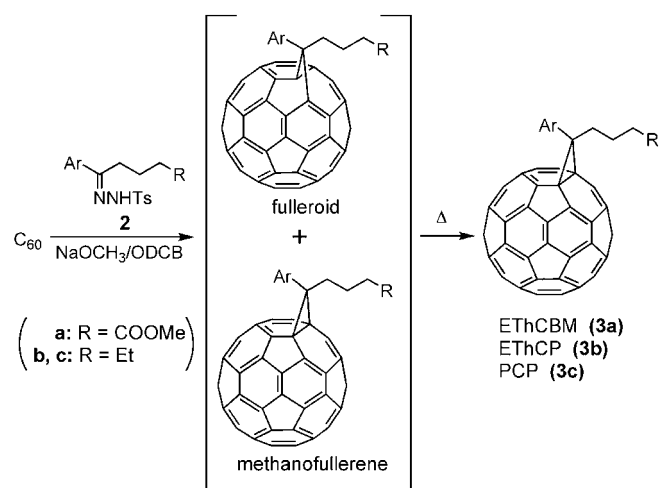
2. Results and discussion

Novel methanofullerenes were synthesized as described in previous papers.[9] Scheme 1 shows the preparation of tosylhy-drasones **2**, the precursors of methanofullerenes. Tosylhydrazones **2a** and **2b** were synthesized by the reaction of *p*-toluenesulfonyl hydrazide (TsNHNH₂) with ketones **1a** and **1b**, respectively, which were obtained by the Friedel–Crafts acylation of commercially available 2-ethylthiophene. Tosylhydrazone **2c** was prepared from commercial phenyl *n*-pentyl ketone as a starting material (Scheme 2).

Scheme 2.

the case of **2c** having a phenyl group, a mixture of [6,6]- and [5,6]-isomers was produced as expected. The production of [5,6]-PCP was confirmed by ^{13}C NMR and the electronic absorption spectra,[10] and the conversion of the [5,6]- to the [6,6]-isomer was accom-plished by heating at 170 °C for 4.5 h. In contrast, only the [6,6]-isomers of EThCBM and EThCP were obtained, and seemed to be thermodynamically more stable than [5,6]-fulleroid, probably because of the strong electron-donating effect of the thienyl substituent.[11]

This reaction gave not only the monoadduct **3** but also bisad-ducts **4**, which contained some regio-isomers, as shown in Scheme 3. The bisadducts **4** were a mixture of regio-isomers and could be confirmed by FD-MS. The total yields of **3** and **4** amounted to approximately 60% of consumed C_{60} as shown in Table 1. The inconsistency of the total yields probably resulted from the production of the multi-adducts, which were separated by preparative GPC.

Scheme 1.

Methanofullerenes were synthesized from C_{60} in the presence of slightly excess amount of tosylhydrazones **2** under basic conditions, while monitoring the reaction by TLC. EThCBM (**3a**) having a bu-tyric acid methyl ester group was easily distinguishable from C_{60} by TLC, similar to the case of PCBM. In the case of EThCP (**3b**) and PCP (**3c**) having an *n*-pentyl group instead of a butyric acid methyl ester group, the R_f values of **3b** and **3c** were unexpectedly close to that of C_{60}. From this result, the methyl ester moiety was obviously found to influence the polarities of methanofullerenes. In particular, the R_f value of PCP (**3c**) has too similar to C_{60} to monitor the reaction by TLC. Hence, the reaction of **2c** was monitored by HPLC with a C-18 column as an eluent (toluene/methanol=50:50). In the case of **3b** and **3c**, preparative gel permeation chromatography (GPC) was used for the isolation of the products.
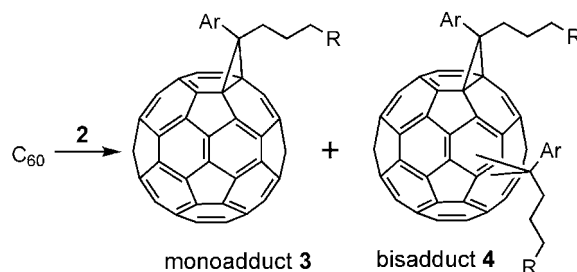
It is well known that the isomers of both [5,6]-fulleroid and [6,6]-methanofullerene are often produced in this reaction, and in

Scheme 3.

Table 1
Reaction conditions and yields for monoadducts **3** and bisadducts **4**

Monoadducts	**2** (equiv)	Conversion of C_{60} (%)	Yields of **3** (%)	Yields of **4** (%)	Total yields of **3** and **4** (%)
EThCBM (**3a**)	1.6	90	38 (42)[a]	21 (23)[a]	59 (66)[a]
EthCP (**3b**)	1.5	95	35 (36)[a]	21 (23)[a]	56 (59)[a]
[6,6]PCP (**3c**)[b]	1.2	98	30 (31)[a]	19 (20)[a]	49 (51)[a]

[a] Based on consumed C_{60}.
[b] Compound **3c** was completely converted from [5,6]-isomer by heating at 170 °C for 4.5 h.

Solubility of the methanofullerenes **3** is one of the most im-portant properties for the fabrication of photovoltaic devices with good performance.[6d] Solubility data were obtained by the absorp-tion spectroscopic technique because of its higher determination

accuracy. Figure 1 shows the electronic absorption spectra of **3**, [5,6]-PCP, and PCBM as comparative samples. All methanofullerenes exhibited a small sharp band at 432 nm and two broad bands around 500 nm and 700 nm, which are characteristic of [6,6]-methanofullerenes. In contrast, the [5,6]-PCP had no characteristic bands in [6,6]-isomer and only one broad band at $\lambda_{max}=542$ nm was observed in the visible region. The solubility in dichloromethane was estimated from the absorbance results in the saturated solution and the extinction coefficient of **3** and PCBM at a λ_{max} of 432 nm, as shown in Table 2.
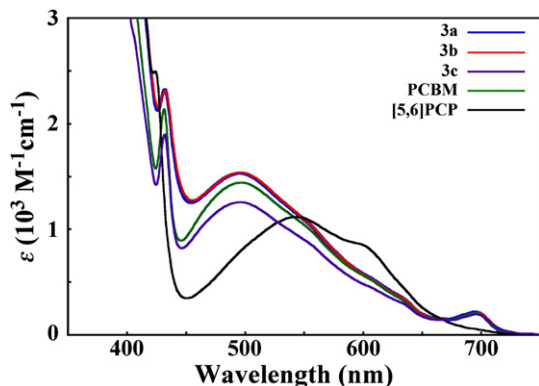

Figure 1. Electronic absorption spectra of **3a**, **3b**, **3c**, PCBM, and [5,6]PCP in a dichloromethane solution.

Table 2
Absorption and solubility of **3**, PCBM, and C_{60} in dichloromethane

Entry	Compound	λ_{max} (nm)	ε ($M^{-1} cm^{-1}$)	Absorbance[a] at λ_{max}	Solubility (g/L)
1	EThCBM (**3a**)	432.0	2326	0.428	8.69
2	EThCP (**3b**)	432.0	2313	0.245	4.87
3	[6,6]PCP (**3c**)	432.0	1897	0.287	6.64
4	PCBM	431.5	2136	0.750	16.0
5	C_{60}	—	—	—	0.26[12]

[a] Measured after diluting the saturated solutions by 50 times.

As a result, significant solubility improvements were confirmed for all of the novel methanofullerene **3** in comparison with that of C_{60} (Table 2, entries 1–3). In particular, the influence of methyl ester group introduced in the methanofullerenes on the solubility was larger than that of the alkyl group. The influences of the 2-ethylthienyl and phenyl substituents were almost similar, but the influence of the phenyl substituent was a little greater than that of 2-ethylthienyl group.

Photovoltaic cells of ITO/(PEDOT:PSS)/(P3HT:methanofullerene)/LiF/Al (methanofullerene=EThCBM (**3a**), EThCP (**3b**), PCP (**3c**), ThCBM, and PCBM) were fabricated, and their performances were listed in Table 3, although these data were not optimized. The conversion efficiency (η) exceeded 2.2% for all of the devices. To our surprise, EThCP and PCP devices showed slightly higher η values than that of PCBM (Table 3, entries 2 and 3).

The conversion efficiency of a solar cell is proportional to the short circuit current (J_{SC}) and open-circuit voltage (V_{OC}), according to the equation of $\eta=FF \cdot J_{SC} \cdot V_{OC}$, where FF is the fill factor. It has been reported in some studies that V_{OC} is related to the difference between the highest occupied molecular orbital (HOMO) of P3HT as the electron donor and the lowest unoccupied molecular orbital (LUMO) of methanofullerene as the electron acceptor, and that the LUMO level of methanofullerene is closely correlated with the electronic properties of the substituents introduced in the parent fullerene.[13] To estimate the LUMO levels of methanofullerenes, their redox behavior was investigated by cyclic voltammetry. All of the methanofullerenes exhibited three or four reversible electroreductions. The first reduction potentials and energy difference between the peak potentials are listed in Table 3. All of the first reduction potentials $E_{1/2,red}$ were located at −1.143 to −1.162 V vs the ferrocene/ferrocenium couple (Fc/Fc⁺). The $E_{1/2,red}$ values of **3b** and **3c**, which had n-pentyl groups, were negatively shifted by 8–19 mV, as compared to the corresponding methanofullerenes **3a**, PCBM, and ThCBM with a methyl ester group (Table 3, entries 2 and 3). From these results, we found that the presence of the ester group lowered the LUMO level of the methanofullerenes to give a smaller V_{OC}. As a result, the V_{OC} values of EThCP and PCP, which have no ester group were larger than that of PCBM.

In relation to J_{SC}, the J_{SC} values of EThCP and PCP were a little higher than that of PCBM. In general, J_{SC} and FF are strongly related to the morphology of the active layer. Although we observed and compared the morphologies of spin-coated P3HT/methanofullerenes surfaces, we could not find a large difference between them and a P3HT/PCBM surface (Fig. 2). The relation between the morphologies and the differences in the molecular structures of the acceptors is still under investigation.

3. Conclusion

In this study, three novel methanofullerenes **3** were designed and synthesized by the reaction of C_{60} with correspondent tosylhydrazones **2** using the method in previous papers. Only in the case of PCP (**3c**) was the [5,6]-fulleroid isomer formed in this reaction at a lower temperature. The solubilities of the novel methanofullerenes were examined in dichloromethane, and it was found that they all had adequate solubilities for fabricating solar cell devices. Bulk-heterojunction solar cells consisting of P3HT and the novel methanofullerenes were fabricated and their performances were evaluated in comparison with those of PCBM and ThCBM devices. As a result, all of the novel methanofullerene devices were found to exhibit conversion efficiencies of over 2.2%, which were superior to a PCBM device. The J_{SC} and V_{OC} values of the devices consisting of EThCP and PCP, which had the n-pentyl group, were found to be higher than those of EThCBM and PCBM, which had the methyl ester group. It is considered that the absence of the ester group raised the LUMO level to give higher V_{OC} values in the case of devices consisting of EThCP and PCP.

Table 3
The work and cyclic voltammetry data summarizing the performance of the manufactured photovoltaic devices

Entry	Methanofullerene	J_{SC} (mA cm⁻²)	V_{OC} (V)	FF	η (%)	$E_{1/2,red}$[a] (V)	ΔE[b] (mV)
1	EThCBM (**3a**)	6.10	0.628	0.587	2.25	−1.147	73
2	EThCP (**3b**)	6.72	0.676	0.568	2.58	−1.162	81
3	PCP (**3c**)	6.79	0.663	0.571	2.57	−1.161	74
4	PCBM	6.12	0.619	0.585	2.22	−1.153	78
5	ThCBM	6.77	0.619	0.601	2.52	−1.143	72

[a] V vs Ferrocene/Ferrocenium couple (Fc/Fc⁺). (n-Bu)₄NClO₄ (0.05 mol dm⁻³) as a supporting electrolyte in ODCB. Scan rate=20 mV s⁻¹.
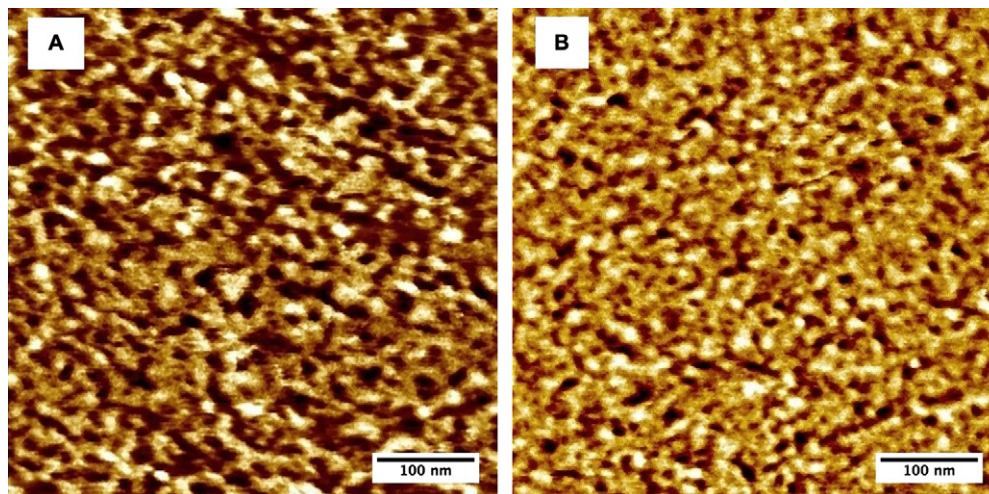[b] An anodic to cathodic peak separation of cyclic voltammogram.

Figure 2. AFM phase images (500×500 nm^2 area) of fabricated P3HT/fullerenes devices containing (A) EThCP and (B) PCP.

4. Experimental

4.1. Reagents and instruments

All of the reagents were purchased and used without further purification. C$_{60}$ was purchased from Honjo Chemical Inc. 1,2-Dichlorobenzene (ODCB) was dried and distilled from calcium hydride. Acetonitrile was dried over molecular sieves (3 Å). Regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT) was purchased from Sigma–Aldrich Corp. Poly(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS) (Baytron P) was provided by H.C. Starck Ltd. Preparative GPC was carried out by Japan Analytical Industry, Co., Ltd. LC-908 with a JAIGEL-1H and a JAIGEL-2H GPC column. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL AL300. FD-mass spectra were obtained on a JEOL JMS-303HF. Electronic absorption spectra were recorded on a Shimadzu Corp. UV-3100A. Cyclic voltammetry was carried out using a BAS Electrochemical Analyzer Model 630A.

4.2. Fabrication of the photovoltaic devices and determination of the device performances

Photovoltaic devices were fabricated from a blend of P3HT as a donor and the methanofullerene (**3a**–**3c**, PCBM, and ThCBM) as an acceptor. The PEDOT:PSS layer was prepared by spin-coating on the top of an indium-tin oxide (ITO) coated glass substrate. Under dry nitrogen, a chlorobenzene solution of the P3HT and methanofullerene in a 1:0.8 w/w ratio was prepared with a 1 wt % methanofullerene concentration. Then the P3HT:methanofullerene blend as the active layer was spin-coated on the PEDOT:PSS layer. After drying the substrates overnight at ambient temperature under nitrogen, a 0.5 nm layer of LiF and a 100 nm layer of Al were deposited on the active layer as the cathode. The devices were encapsulated with a glass plate and epoxy resin to avoid exposure to the air and moisture after all lamination processes. The device performance was determined by a solar simulator under simulated solar illumination (AM1.5G, 100 mW cm^{-2}). The reproducibility of the measurements was confirmed with three devices for each sample and the highest performance was shown. After the measurements, AFM images of the active layers were taken with a Digital Instruments Nanoscope IIIa at a scan rate of 1.0 Hz in the tapping mode. Cyclic voltammetry measurements were performed at ambient temperature under an argon atmosphere in a 0.1 mol dm^{-3} ODCB solution of tetra-n-butylammonium

perchlorate using a Pt electrode as a working electrode and a platinum wire as a counter electrode with approximately 2.5×10^{-1} mol dm^{-3} of the samples. The reference electrode was an Ag/AgNO$_3$ electrode filled with 0.1 mol dm^{-3} of (n-Bu)$_4$NClO$_4$ in acetonitrile. All of the potentials were referenced to the ferrocene/ferrocenium couple (Fc/Fc$^+$) as an internal standard. CV measurements were performed three times on each samples and the mean value of them were shown.

4.3. Synthesis

*4.3.1. 5-Ethylthiophene-2-yl (3-methoxycarbonyl)propyl ketone (**1a**).* 2-Ethylthiophene (5.0 g, 45 mmol), methyl 5-chloro-5-oxovalerate (8 g, 49 mmol), and aluminum chloride anhydrous (0.6 g, 4.5 mmol) were dissolved in 40 mL of dry acetonitrile, followed by heating to the reflux temperature and stirring for 8 h. After the reaction mixture was cooled to room temperature, it was poured into 1 L of 1 wt % NaOH aqueous solution and extracted with toluene. The organic layer was dried over MgSO$_4$ and concentrated in vacuo to give a crude product. The purified product was obtained by silicagel column chromatography using toluene as an eluent. Isolated yield=49% (5.3 g); brown oil; HRMS (MALDI TOF): m/z [M+H$^+$] calcd for C$_{12}$H$_{17}$O$_3$S: 241.0898; found: 241.0896; ^{1}H NMR (acetone-d_6): δ 7.58 (d, 1H, 9.0 Hz), 6.80 (d, 1H, 9.3 Hz), 3.49 (s, 3H), 2.88–2.72 (m, 4H), 2.25 (t, 2H, 5.4 Hz), 1.83 (tt, 2H, 2.4 Hz), 1.15 (t, 3H, 6.5 Hz); ^{13}C NMR (acetone-d_6): δ 192.47, 173.77, 157.42, 142.69, 133.46, 126.05, 51.53, 38.03, 33.48, 24.38, 20.62, 15.96.

*4.3.2. Methyl 5-(5-ethylthiophene-2-yl)-5-(2-tosylhydrazono)-valerate (**2a**).* Compound **1a** (4.7 g, 20 mmol) and p-toluenesulfonehydrazide (4.5 g, 24 mmol) were dissolved in 50 mL of methanol, followed by heating to the reflux temperature and stirring for 24 h. The reaction mixture was cooled to room temperature to give a precipitate of product, and the precipitate was collected and recrystallized from methanol. Isolated yield=74% (5.9 g); light yellow crystal: mp 117–119 °C; MALDI TOF-MS: m/z 410 (M+H)$^+$; ^{1}H NMR (CDCl$_3$): δ 9.32 (s, 1H), 7.81 (d, 2H, 8.4 Hz), 7.38 (d, 2H, 8.1 Hz), 7.21 (d, 1H, 3.6 Hz), 6.73 (d, 1H, 3.6 Hz), 3.65 (s, 3H), 2.83–2.69 (m, 6H), 2.37 (t, 3H, 6.9 Hz), 1.78 (tt, 2H, 6.9 Hz), 1.29 (t, 3H, 7.5 Hz); ^{13}C NMR (CDCl$_3$): δ 174.24, 152.55, 151.24, 144.51, 140.58, 137.49, 130.17, 128.81, 128.07, 124.67, 51.85, 33.25, 27.01, 24.11, 22.37, 21.40, 16.05; IR (KBr): 3187, 2960, 2935, 1715, 1592, 1405, 1341, 1306, 1224, 1164, 1021, 985, 914, 870, 815, 801, 704, 676,

577, 549, 517 cm^{-1}. Anal. Calcd for C$_{19}$H$_{24}$N$_2$O$_4$S$_2$: C, 55.86; H, 5.92; N, 6.86; O, 15.67; S, 15.70. Found: C, 55.95; H, 6.01; N, 6.89.

4.3.3. 1-(5-Ethylthiophene-2-yl)-1-(3-methoxycarbonyl)propyl-[6,6]-methanofullerene[60] (EThCBM) (**3a**) and bis-adduct **4a**.

C$_{60}$ (300 mg, 0.42 mmol) was dissolved in 9 mL of dry ODCB by ultrasonic treatment for 60 min at ambient temperature under Ar. Into the solution, 1.6 equiv of **2a** (272 mg, 0.67 mmol), 1.6 equiv of sodium methoxide (36 mg, 0.67 mmol), and 6 mL of dry pyridine were added. The mixture was stirred at 70 °C for 1 h and 100 °C for 1 h. After removal of the solvent by distillation, the residue was purified by silicagel column chromatography with toluene to give EThCBM. Isolated yield=38% (150 mg, 42%; based on consumed C$_{60}$); brown powder; UV–vis (CH$_2$Cl$_2$) λ_{max}=432 nm (ε=2326); HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{72}$H$_{16}$O$_2$S: 944.0871; found: 944.0866; ^{1}H NMR (CDCl$_3$): δ 7.27 (d, 1H, 3.60 Hz), 6.78 (d, 1H, 3.60 Hz), 3.69 (s, 3H), 2.99–2.90 (m, 4H), 2.58 (t, 2H, 7.5 Hz), 2.29–2.19 (m, 2H), 1.41 (t, 3H, 7.5 Hz); ^{13}C NMR (CDCl$_3$): δ 173.50, 148.50, 148.40, 147.65, 145.74, 145.23, 145.20, 145.18, 145.13, 144.81, 144.72, 144.64, 144.57, 144.47, 144.14, 143.82, 143.78, 143.10, 143.04, 143.00, 142.92, 142.90, 142.26, 142.17, 142.13, 142.11, 140.92, 140.70, 138.26, 138.10, 135.97, 131.77, 122.20, 80.08, 51.66, 46.20, 33.86, 33.71, 23.68, 22.52, 15.53; IR (KBr): 2960, 2328, 1737, 1456, 1428, 1376, 1263, 1186, 1170, 983, 885, 806, 741, 572, 562, 525, 445 cm^{-1}.

Bis-adduct **4a**, mixture of regioisomer, was successfully separated from the residue by preparative GPC and identified by high-resolution mass spectrometry. Isolated yield=21% (103 mg, 23%; based on consumed C$_{60}$); brown powder; HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{84}$H$_{32}$O$_4$S$_2$: 1168.1742; found: 1168.1770.

4.3.4. 5-Ethylthiophene-2-yl n-pentyl ketone (**1b**).

2-Ethylthiophene (6.7 g, 60 mmol), *n*-hexanoyl chloride (8.5 g, 63 mmol), and aluminum chloride anhydrous (0.8 g, 6 mmol) were dissolved in 60 mL of dry acetonitrile, followed by heating to the reflux temperature and stirring for 8 h. After the reaction mixture was cooled to room temperature, it was poured into 1 L of 1 wt % NaOH aqueous solution and extracted with toluene. The organic layer was dried over MgSO$_4$ and concentrated in vacuo to give a crude product. The purified product was obtained by silicagel column chromatography using 30 vol % of *n*-hexane in toluene as an eluent. Yield 67% (8.5 g); brown oil; HRMS (MALDI TOF): m/z [M+H$^+$] calcd for C$_{12}$H$_{19}$OS: 211.1157; found: 211.1148; ^{1}H NMR (acetone-d_6): δ 7.68 (d, 1H, 3.9 Hz), 6.93 (d, 1H, 3.9 Hz), 2.93–2.85 (m, 4H), 1.68 (tt, 2H, 2.1 Hz), 1.38–1.28 (m, 7H), 0.90 (t, 3H, 6.9 Hz); ^{13}C NMR (acetone-d_6): δ 193.03, 157.16, 142.96, 133.19, 125.95, 39.00, 32.15, 25.15, 24.38, 23.13, 15.96, 14.21.

4.3.5. 1-(5-Ethylthiophene-2-yl)-1-(2-tosylhydrazono)pentane (**2b**).

Compound **1b** (4.2 g, 20 mmol) and *p*-toluenesulfonehydrazide (4.5 g, 24 mmol) were dissolved in 50 mL of methanol, followed by heating to the reflux temperature and stirring for 24 h. The reaction mixture was cooled to room temperature to give a precipitate of product, and the precipitate was collected and recrystallized from methanol. Isolated yield=83% (6.3 g); colorless crystal: mp 132–134 °C; MALDI TOF-MS: 379 (M+H)$^+$; ^{1}H NMR (CDCl$_3$): δ 7.91 (t, 3H, 8.1 Hz), 7.29 (t, 2H, 8.1 Hz), 6.99 (d, 1H, 3.6 Hz), 6.64 (d, 1H, 3.6 Hz), 2.79 (q, 2H, 7.8 Hz), 2.50 (t, 2H, 8.0 Hz), 2.40 (s, 3H), 1.53–1.32 (m, 2H), 1.29–1.19 (m, 7H), 0.82 (t, 3H, 6.9 Hz); ^{13}C NMR (CDCl$_3$): δ 153.01, 150.91, 144.00, 139.62, 135.39, 129.53, 128.21, 126.66, 123.48, 31.76, 27.49, 26.04, 23.74, 22.42, 15.67, 13.83; IR (KBr): 3215, 2926, 2858, 1595, 1480, 1381, 1343, 1168, 1026, 918, 816, 802, 665, 570, 547 cm^{-1}. Anal. Calcd for C$_{19}$H$_{26}$N$_2$O$_2$S$_2$: C, 60.28; H, 6.92; N, 7.40; O, 8.45; S, 16.94. Found: C, 60.12; H, 6.90; N, 7.39.

4.3.6. 1-(5-Ethylthiophene-2-yl)-1-(n-pentyl)-[6,6]-methanofullerene[60] (EThCP) (**3b**) and bis-adduct **4b**.

C$_{60}$ (100 mg, 0.14 mmol) was dissolved in 3 mL of dry ODCB by ultrasonic treatment for 60 min at ambient temperature under Ar. Into the solution, 1.5 equiv of **2b** (79 mg, 0.21 mmol), sodium methoxide (12 mg, 0.22 mmol), and 2 mL of dry pyridine were added. The mixture was stirred at 70 °C for 1 h and 100 °C for 1 h. After removal of the solvent by distillation, the residue was purified by preparative gel permeation chromatography with chloroform to give EThCP. Isolated yield=35% (44 mg, 36%; based on consumed C$_{60}$); brown powder; UV–vis (CH$_2$Cl$_2$) λ_{max}=432 nm (ε=2313): HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{72}$H$_{18}$S: 914.1129; found: 914.1151; ^{1}H NMR (CDCl$_3$): δ 7.24 (d, 1H, 3.6 Hz), 6.78 (d, 1H, 3.6 Hz), 2.99–2.84 (m, 4H) 1.95–1.85 (m, 2H), 1.55–1.48 (m, 4H), 1.41 (t, 3H, 7.5 Hz), 0.94 (t, 3H, 7.2 Hz); ^{13}C NMR (CDCl$_3$): δ 148.91, 148.18, 145.88, 145.32, 145.28, 145.25, 145.20, 144.90, 144.87, 144.85, 144.73, 144.64, 144.51, 144.19, 143.91, 143.89, 143.19, 143.12, 143.08, 143.00, 142.98, 142.39, 142.32, 142.22, 141.00, 140.77, 138.32, 138.19, 136.74, 131.57, 122.10, 80.73, 47.17, 34.58, 31.70, 26.85, 23.71, 22.67, 15.57, 14.03; IR (KBr): 2952, 2921, 2852, 2359, 1427, 1375, 1186, 805, 740, 574, 555, 526, 451 cm^{-1}.

Bis-adduct **4b**, mixture of regioisomer, was successfully separated from the residue by preparative GPC with chloroform and identified by high-resolution mass spectrometry. Yield=21% (33 mg, 23%; based on consumed C$_{60}$); brown powder; HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{84}$H$_{36}$S$_2$: 1108.2258; found: 1108.2258.

4.3.7. 1-Phenyl-1-(2-tosylhydrazono)pentane (**2c**).

n-Hexanophenone (3.5 g, 20 mmol) and *p*-toluenesulfonehydrazide (4.5 g, 24 mmol) were dissolved in 50 mL of methanol, followed by heating to the reflux temperature and stirring for 24 h. The reaction mixture was cooled to room temperature to give a precipitate of product, and the precipitate was collected and recrystallized from methanol. Isolated yield=67% (4.6 g); colorless crystal: mp 112–114 °C; MALDI TOF-MS: 345 (M+H)$^+$; ^{1}H NMR (CDCl$_3$): δ 7.93–7.86 (m, 3H), 7.64–7.60 (m, 2H), 7.35–7.25 (m, 5H), 2.55 (t, 2H, 8.0 Hz), 2.41 (s, 3H), 1.45 (tt, 2H, 7.7 Hz), 1.30–1.24 (m, 4H), 0.83 (t, 3H, 7.1 Hz); ^{13}C NMR (CDCl$_3$): δ 158.43, 155.96, 144.11, 136.51, 135.51, 129.62, 129.54, 129.53, 128.56, 128.40, 128.32, 126.72, 126.40, 31.85, 26.79, 25.58, 22.41, 21.60, 13.85; IR (KBr): 3210, 2951, 2868, 1596, 1474, 1446, 1385, 1342, 1168, 1065, 928, 816, 754, 687, 667, 611, 545, 529 cm^{-1}. Anal. Calcd for C$_{19}$H$_{24}$N$_2$O$_2$S: C, 66.25; H, 7.02; N, 8.13; O, 9.29; S, 9.31. Found: C, 65.96; H, 7.11; N, 8.04.

4.3.8. 1-n-Pentyl-1-phenyl-[5,6]-methanofullerene[60] ([5,6]PCP) and bis-adduct **4c**.

C$_{60}$ (100 mg, 0.14 mmol) was dissolved in 3 mL of dry ODCB by ultrasonic treatment for 60 min at ambient temperature under Ar. Into the solution, 1.2 equiv of **2c** (58 mg, 0.17 mmol), sodium methoxide (9 mg, 0.17 mmol), and 2 mL of dry pyridine were added. The mixture was stirred at 70 °C for 1 h and 100 °C for 0.5 h. After removal of the solvent by distillation, the residue was purified by preparative gel permeation chromatography with chloroform to give [5,6]PCP. Isolated yield=31% (38 mg, 32%; based on consumed C$_{60}$); brown powder; UV–vis (CH$_2$Cl$_2$) λ_{max}=542.5 nm (ε=1118); HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{72}$H$_{16}$: 880.1252; found: 880.1255; ^{1}H NMR (CDCl$_3$): δ 7.97–7.94 (m, 2H), 7.55 (t, 2H, 8.1 Hz), 7.43 (tt, 1H, 9.3 Hz), 1.62–1.57 (m, 2H), 1.21–1.08 (m, 6H), 0.79 (t, 3H, 6.9 Hz); ^{13}C NMR (CDCl$_3$): δ 147.43, 147.00, 145.19, 144.75, 144.49, 144.23, 143.96, 143.75, 143.69, 143.55, 143.13, 143.08, 143.07, 142.97, 142.69, 142.65, 142.58, 142.13, 142.10, 141.93, 141.83, 141.33, 140.96, 140.44, 139.81, 138.80, 138.62, 138.11, 137.91, 136.65, 135.10, 130.83, 128.48, 127.52, 61.64, 36.10, 31.84, 23.83, 22.35, 13.94; IR (KBr): 2950, 2923, 2855, 2331, 1599, 1509, 1444, 1427, 1382, 1189, 1173, 1118, 1077, 1029, 753, 720, 697, 642, 612, 581, 572, 543, 526 cm^{-1}.

Bis-adduct **4c**, mixture of regioisomer, was successfully separated from the residue by preparative GPC and identified by high-resolution mass spectrometry. Isolated yield=19% (28 mg, 20%; based on consumed C$_{60}$); brown powder; HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{84}$H$_{32}$: 1040.2504; found: 1040.2540.

4.3.9. 1-n-Pentyl-1-phenyl-[6,6]-methanofullerene[60] ([6,6]PCP) (3c). [5,6]-PCP (38 mg, 0.044 mmol) was dissolved in 3 mL of ODCB followed by heating to 170 °C, and stirring for 4.5 h. After removal of the solvent by distillation, the residue was purified by preparative gel permeation chromatography with chloroform to give [6,6]PCP. Isolated yield=97% (37 mg); brown powder; UV–vis (CH$_2$Cl$_2$) λ_{max}=432 nm (ε=1897); HRMS (MALDI TOF): m/z [M$^-$] calcd for C$_{72}$H$_{16}$: 880.1252; found: 880.1250; ^{1}H NMR (CDCl$_3$): δ 7.84 (d, 2H, 6.9 Hz), 7.48–7.35 (m, 3H), 2.80 (t, 2H, 8.1 Hz), 1.82–1.72 (m, 2H), 1.46–1.26 (m, 4H), 0.84 (t, 3H, 7.2 Hz); ^{13}C NMR (CDCl$_3$): δ 149.17, 148.30, 146.00, 145.25, 145.20, 145.09, 144.90, 144.85, 144.80, 144.74, 144.56, 144.43, 144.04, 143.85, 143.20, 143.09, 143.06, 143.00, 142.37, 142.29, 142.21, 141.04, 140.78, 138.10, 137.59, 137.37, 132.18, 128.28, 128.06, 80.47, 52.77, 34.33, 31.86, 26.70, 22.63, 14.02; IR (KBr): 2961, 2918, 2856, 2328, 1599, 1493, 1426, 1260, 1185, 1092, 1019, 866, 799, 694, 585, 573, 548, 526 cm^{-1}.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.06.089.

References and notes

1. Zhao, J.; Wang, A.; Green, M. A. *Appl. Phys. Lett.* **1998**, *73*, 1991.
2. Shaheen, S. E.; Brabec, C. J.; Sariciftci, N. S.; Padinger, F.; Fromherz, T.; Hummelen, J. C. *Appl. Phys. Lett.* **2001**, *78*, 841.
3. (a) Sirringhaus, H.; Tessler, N.; Friend, R. H. *Science* **1998**, *280*, 1741; (b) Vissenberg, M. C. J. M.; Matters, M. *Phys. Rev. B* **1998**, *57*, 12964.
4. (a) Martens, T.; D'Haen, J.; Munters, T.; Beelen, Z.; Goris, L.; Manca, J.; D'Olieslaeger, M.; Vanderzand, D.; Schepper, L. D.; Andriessen, R. *Synth. Met.* **2003**, *138*, 243; (b) Li, G.; Shrotoriya, V.; Huang, J.; Yao, Y.; Moriarty, T.; Emery, K.; Yang, Y. *Nat. Mater.* **2005**, *4*, 864; (c) Hayakawa, A.; Yoshikawa, O.; Fujieda, T.; Uehara, K.; Yoshikawa, S. *Appl. Phys. Lett.* **2007**, *90*, 163517.
5. (a) Hou, J.; Tan, Z.; Yan, Y.; He, Y.; Yang, C.; Li, Y. *J. Am. Chem. Soc.* **2006**, *128*, 4911; (b) Zhou, E.; He, C.; Tan, Z.; Yang, C.; Li, Y. *J. Polym. Sci., Part A* **2006**, *44*, 4916; (c) Winder, C.; Sariciftci, N. S. *J. Mater. Chem.* **2004**, *14*, 1077; (d) Brabec, C. J.; Winder, C.; Sariciftci, N. S.; Hummelen, J. C.; Dhanabalan, A.; Hal, P. A.; van; Janssen, R. A. J. *Adv. Funct. Mater.* **2002**, *12*, 709; (e) Zhang, F.; Jespersen, K. G.; Björström, C.; Svensson, M.; Andersson, M. R.; Sundström, V.; Magnusson, K.; Moons, E.; Yartsev, A.; Inganäs, O. *Adv. Funct. Mater.* **2006**, *16*, 667; (f) Gardisa, A.; Zhang, F.; Sharma, D.; Svwnsson, M.; Andersson, M. R.; Inganäs, O. *Thin Solid Films* **2007**, *515*, 3126; (g) Zhang, F.; Mammo, W.; Andersson, L. M.; Admassie, S.; Andersson, M. R.; Inganäs, O. *Adv. Mater.* **2006**, *18*, 2169; (h) Shi, C.; Yao, Y.; Yang, Y.; Pei, Q. *J. Am. Chem. Soc.* **2006**, *128*, 8980; (i) Wienk, M. M.; Turbiez, M. G. R.; Struijk, M. P.; Fonrodona, M.; Janssen, R. A. J. *Appl. Phys. Lett.* **2006**, *88*, 153511; (j) Mühlbacher, D.; Scharber, M.; Morana, M.; Zhu, Z.; Waller, D.; Gaudiana, R.; Brabec, C. *Adv. Mater.* **2006**, *18*, 2884; (k) Soci, C.; Hwang, I.-W.; Moses, D.; Zhu, Z.; Waller, D.; Guadiana, R.; Brabec, C. J.; Heeger, A. J. *Adv. Funct. Mater.* **2007**, *17*, 632.
6. (a) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Fromherz, T.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C. *Adv. Funct. Mater.* **2002**, *11*, 374; (b) Brabec, C. J.; Cravino, A.; Meissner, D.; Sariciftci, N. S.; Rispens, M. T.; Sanchez, L.; Hummelen, J. C.; Fromherz, T. *Thin Solid Films* **2002**, *403-404*, 368; (c) Riedel, I.; Martin, N.; Giacalone, F.; Segura, J. L.; Chirvase, D.; Parisi, J.; Dyakonov, V. *Thin Solid Films* **2004**, *451-452*, 43; (d) Troshin, P. A.; Hoppe, H.; Renz, J.; Egginger, M.; Mayorova, J. Y.; Goryachev, A. E.; Peregudov, A. S.; Lyubovskaya, R. N.; Gobsch, G.; Sariciftci, N. S.; Razumov, V. F. *Adv. Funct. Mater.* **2009**, *19*, 779.
7. Popescu, L. M.; van't Hof, P.; Sieval, A. B.; Jonkman, H. T.; Hammelen, J. C. *Appl. Phys. Lett.* **2006**, *89*, 213507.
8. Matsumoto, F.; Moriwaki, K.; Takao, Y.; Ohno, T. *Beilstein J. Org. Chem.* **2008**, *4*, 33.
9. (a) Hummelen, J. C.; Knight, B. W.; LePeq, F.; Wudl, F.; Yao, J.; Wilkins, C. L. *J. Org. Chem.* **1995**, *60*, 532; (b) Ohno, T.; Moriwaki, K.; Miyata, T. *J. Org. Chem.* **2001**, *66*, 3397.
10. Prato, M.; Lucchini, V.; Maggini, M.; Stimpfl, E.; Scorrano, G.; Eiermann, M.; Suzuki, T.; Wudl, F. *J. Am. Chem. Soc.* **1993**, *115*, 8479.
11. (a) Suzuki, T.; Li, Q.; Khemani, K. C.; Wudl, F. *J. Am. Chem. Soc.* **1992**, *114*, 7301; (b) Hall, M. H. *J. Org. Chem.* **2006**, *71*, 3357; (c) Kitamura, H.; Kokubo, K.; Oshima, T. *Org. Lett.* **2007**, *9*, 4045.
12. (a) Scrivens, W. A.; Tour, J. M. *J. Chem. Soc., Chem. Commun.* **1993**, 1207; (b) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, D. C. *J. Phys. Chem.* **1993**, *97*, 3379.
13. (a) Kooistra, F. B.; Knol, J.; Kastenberg, F.; Popescu, L. M.; Verhees, W. J. H.; Kroon, J. M.; Hummelen, J. C. *Org. Lett.* **2007**, *9*, 551; (b) Morvillo, P.; Bobeico, E. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1192.