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

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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, their poor cost performance and the unstable supply of silicon have prevented the extensive usage 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'-dimethoxycarbonyl)-1,4-phenylenevinylene] (MDMO-PPV),\(^5\) 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.\(^6\)

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\(_{61}\)-butyric 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\(_{61}\)-butyric 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] (3\(b\)) and 1-phenyl-[6,6]-methanofullerene[60] (3\(c\)) were negatively shifted compared to those of the corresponding terminal methyl ester-substituted homologues (3\(a\) and PCBM). The performances of photovoltaic devices consisting of 3\(b\) and 3\(c\) were slightly higher than those of PCBM.

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Recently, Hummelen et al. reported a device fabricated with a thiényl analogue, ThCBM, 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 thiényl groups and investigated their structural effect on the solubilities and morphologies of their mixtures with P3HT. 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 methanofullerenes. 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-ethylthiényl) 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/methanofullerene devices having much higher performance than a P3HT/PCBM system and acquiring a guideline for designing optimum molecular structures for them. The 2-(5-ethylthiényl) group was selected instead of thiényl group because of stabilization of the oxidizable x-proton of thiophene by alkylation. We investigated the basic properties, such as the electronic absorption spectra, solubility of these novel methanofullerenes, and performance of photovoltaic devices that consisted of P3HT and these methanofullerenes.

2. Results and discussion

Novel methanofullerenes were synthetized as described in previous papers. Scheme 1 shows the preparation of tosylhydrazones 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 1](image1)

Methanofullerenes were synthetized from C60 in the presence of slightly excess amount of tosylhydrazones 2 under basic conditions, while monitoring the reaction by TLC. ETHCBM (3a) having a butyric acid methyl ester group was easily distinguishable from C60 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 Rf values of 3b and 3c were unexpectedly close to that of C60. From this result, the methyl ester moiety was obviously found to influence the polarities of methanofullerenes. In particular, the Rf value of PCP (3c) has too similar to C60 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 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 13C NMR and the electronic absorption spectra, and the conversion of the [5,6]- to the [6,6]-isomer was accomplished 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 thiényl substituent.

This reaction gave not only the monoadduct 3 but also bisadducts 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 C60 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 2](image2)

![Scheme 3](image3)

![Scheme 4](image4)

Table 1
<table>
<thead>
<tr>
<th>Monoadducts</th>
<th>Yields (%)</th>
<th>Total yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3a 1a</td>
<td>1.6</td>
<td>90</td>
</tr>
<tr>
<td>3a 1b</td>
<td>1.5</td>
<td>95</td>
</tr>
<tr>
<td>3b 2a</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>3c 2a</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>3c 2b</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>3c 2c</td>
<td>1.2</td>
<td>98</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bisadducts</th>
<th>Yields (%)</th>
<th>Total yields (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4a 1a</td>
<td>1.6</td>
<td>90</td>
</tr>
<tr>
<td>4a 1b</td>
<td>1.5</td>
<td>95</td>
</tr>
<tr>
<td>4b 2a</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>4b 2b</td>
<td>1.2</td>
<td>98</td>
</tr>
<tr>
<td>4b 2c</td>
<td>1.2</td>
<td>98</td>
</tr>
</tbody>
</table>

a. Based on consumed C60. 

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 important properties for the fabrication of photovoltaic devices with good performance. Solubility data were obtained by the absorption spectroscopic techniques 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 \( \lambda_{\text{max}} = 542 \) 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 \( \lambda_{\text{max}} \) 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\textsubscript{60} in dichloromethane

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>( \lambda_{\text{max}} ) (nm)</th>
<th>( e ) (M(^{-1})cm(^{-1}))</th>
<th>Absorbance(^a) at ( \lambda_{\text{max}} )</th>
<th>Solubility (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ETHCBM (3a)</td>
<td>432.0</td>
<td>2326</td>
<td>0.428</td>
<td>8.69</td>
</tr>
<tr>
<td>2</td>
<td>ETHCP (3b)</td>
<td>432.0</td>
<td>2313</td>
<td>0.245</td>
<td>4.87</td>
</tr>
<tr>
<td>3</td>
<td>[6,6]PCP (3c)</td>
<td>432.0</td>
<td>1897</td>
<td>0.287</td>
<td>6.64</td>
</tr>
<tr>
<td>4</td>
<td>PCBM</td>
<td>431.5</td>
<td>2136</td>
<td>0.750</td>
<td>16.0</td>
</tr>
<tr>
<td>5</td>
<td>C\textsubscript{60}</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.26(^1)</td>
</tr>
</tbody>
</table>

\(^a\) Measured after diluting the saturated solutions by 50 times.

As a result, significant solubility improvements were confirmed for all of the novel methanofullerenes 3 in comparison with that of C\textsubscript{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-ethylthiényl and phenyl substituents were almost similar, but the influence of the phenyl substituent was a little greater than that of 2-ethylthiényl group.

As a result of the above, signiﬁcant solubility improvements were conﬁrmed for all of the novel methanofullerenes 3 in comparison with that of C\textsubscript{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-ethylthiényl and phenyl substituents were almost similar, but the influence of the phenyl substituent was a little greater than that of 2-ethylthiényl group.

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Methanofullerene</th>
<th>( J_{SC} ) (mA cm(^{-2}))</th>
<th>( V_{OC} ) (V)</th>
<th>FF</th>
<th>( \eta ) (%)</th>
<th>( E_{1/2,\text{red}} ) (V)</th>
<th>( \Delta E ) (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ETHCBM (3a)</td>
<td>6.10</td>
<td>0.628</td>
<td>0.587</td>
<td>2.25</td>
<td>$-1.147$</td>
<td>73</td>
</tr>
<tr>
<td>2</td>
<td>ETHCP (3b)</td>
<td>6.72</td>
<td>0.676</td>
<td>0.568</td>
<td>2.17</td>
<td>$-1.162$</td>
<td>81</td>
</tr>
<tr>
<td>3</td>
<td>PCP (3c)</td>
<td>6.79</td>
<td>0.663</td>
<td>0.571</td>
<td>2.57</td>
<td>$-1.161$</td>
<td>74</td>
</tr>
<tr>
<td>4</td>
<td>PCBM</td>
<td>6.12</td>
<td>0.619</td>
<td>0.585</td>
<td>2.22</td>
<td>$-1.153$</td>
<td>78</td>
</tr>
<tr>
<td>5</td>
<td>ThCBM</td>
<td>6.77</td>
<td>0.619</td>
<td>0.601</td>
<td>2.52</td>
<td>$-1.143$</td>
<td>72</td>
</tr>
</tbody>
</table>

\(^a\) V vs Ferrocene/Ferrocenium couple (Fc/Fc\(^+\)). (n-Bu\(_4\)N)\textsubscript{4}ClO\(_4\) (0.05 mol dm\(^{-3}\)) as a supporting electrolyte in ODCB. Scan rate=20 mV s\(^{-1}\).

3. Conclusion

In this study, three novel methanofullerenes 3 were designed and synthesized by the reaction of C\textsubscript{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 methanofullerenes 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.
4. Experimental

4.1. Reagents and instruments

All of the reagents were purchased and used without further purification. C60 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-diyi) (P3HT) was purchased from Sigma–Aldrich Corp. Poly(3,4-ethylendioxythiophene):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. 1H NMR and 13C NMR spectra were recorded on a JEOL JMS-303HF. Electronic absorption spectra were recorded on a Shimadzu Corp. UV-3100A. 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 TbCBM) 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% dry nitrogen, a chlorobenzene (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-ethylendioxythiophene):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. 1H NMR and 13C NMR spectra were recorded 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.

4.3. 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 MgSO4 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 C12H17O3S: 241.0898; found: 241.0896; 1H NMR (acetone-d6): 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); 13C NMR (acetone-d6): 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-toluene sulfonylhydrazide (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)+; 1H NMR (CDCl3): 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), 6.75 (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); 13C NMR (CDCl3): δ 174.24, 152.55, 151.24, 144.51, 140.58, 137.49, 130.17, 128.81, 128.07, 124.67, 113.5, 107.8, 105.16, 78.2, 67.7, 35.5, 22.3. 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 2.5×10−4 mol dm−3 of the samples. The reference electrode was an Ag/AgNO3 electrode filled with 0.1 mol dm−3 of (n-Bu4N)NO3 in acetonitrile. All of the potentials were referenced to the ferrocene/ferroacenium couple (Fc/Fc+) as an internal standard. CV measurements were performed three times on each samples and the mean value of them were shown.

Figure 2. AFM phase images (500×500 nm² area) of fabricated P3HT/fullerene devices containing (A) ETHCP and (B) PCP.
577, 549, 517 cm⁻¹. Anal. Calcd for C₆₀H₂₃NO₂S₂: 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. 1-(5-Ethylthiophene-2-yl)-1-(3-methoxycarbonyl)propyl- [6,6]-methanofullerene[60] (ETCBM) (3a) and bis-adduct 4a. C₆₀ (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 preparative gel permeation chromatography with chloroform to give ETCBM. Isolated yield=38% (150 mg, 42%; based on consumed C₆₀); brown powder; UV–vis (CHCl₃) λmax=432 nm (ε=2336); HRMS (MALDI TOF): m/z [M⁺] calc for C₆₄H₆₃O₃S: 944.0871; found: 944.0866; ¹H NMR (CDCl₃): δ 7.27 (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). ¹³C NMR (CDCl₃): 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, 143.89, 143.19, 143.12, 143.08, 143.00, 142.98, 142.39, 142.32, 142.22, 141.00, 147.38, 133.82, 131.19, 131.57, 122.10, 80.73, 47.17, 34.58, 31.70, 26.85, 23.71, 22.67, 15.57, 14.03; IR (KBr): 2929, 2921, 2852, 2399, 1427, 1375, 1186, 805, 740, 574, 555, 526, 451 cm⁻¹.

Bis-adduct 4b, mixture of regiosomer, 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 C₆₀); brown powder; HRMS (MALDI TOF): m/z [M⁺] calc for C₆₄H₆₃O₃S: 1108.2258; found: 1108.2258.

4.3.7. 1-Phenyl-1-(2-isothylhydrazono)pentane (2c). N-hexanophene (3.5 g, 20 mmol) and p-toluenesulfonylhydrazide (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)+; ¹H NMR (CDCl₃): 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 (t, 2H, 7.7 Hz), 1.30–1.24 (m, 4H), 0.83 (t, 3H, 7.1 Hz); ¹³C NMR (CDCl₃): δ 158.43, 155.96, 144.11, 136.51, 135.29, 132.69, 125.92, 125.83, 128.40, 128.32, 127.62, 126.40, 31.85, 26.79, 25.58, 22.41, 21.60, 13.85; IR (KBr): 3210, 2951, 2868, 1596, 1474, 1446, 1385, 1324, 1168, 1065, 928, 816, 754, 687, 667, 611, 545, 529 cm⁻¹. Anal. Calcld for C₁₉H₂₄N₂O₂S: C, 66.25; H, 7.02; N, 8.13; O; 9.29; S. 6.39. Found: C, 65.96; H, 7.11; N, 8.04.

4.3.8. 1-n-Pentyl-1-phenyl-[6,6]-methanofullerene[60] ([6,6]PCP) and bis-adduct 4c. C₆₀ (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 [6,6]PCP. Isolated yield=31% (38 mg, 32%; based on consumed C₆₀); brown powder; UV–vis (CHCl₃) λmax=542.5 nm (ε=1118); HRMS (MALDI TOF): m/z [M⁺] calc for C₂₃H₈₀O₂S: 880.1252; found: 880.1255; ¹H NMR (CDCl₃): δ 7.97–7.94 (m, 2H), 2.75 (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, 9.3 Hz); ¹³C NMR (CDCl₃): δ 147.43, 147.00, 141.95, 147.75, 144.49, 144.23, 143.96, 143.75, 143.69, 143.55, 143.13, 143.08, 142.07, 142.97, 142.69, 142.65, 142.58, 142.12, 141.93, 141.83, 141.30, 140.96, 140.44, 139.81, 138.00, 138.62, 138.11, 137.91, 136.65, 135.10, 130.83, 128.48, 127.52, 61.64, 36.10, 31.84, 23.83, 23.25, 13.94; IR (KBr): 2950, 2925, 2853, 2331, 1599, 1509, 1444, 1427, 1382, 1189, 1173, 1107, 1079, 753, 720, 697, 642, 612, 581, 572, 543, 526 cm⁻¹.

Bis-adduct 4c, mixture of regiosomer, 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 C₆₀); brown powder; HRMS (MALDI TOF): m/z [M⁺] calc for C₃₉H₄₃O₂S: 1040.2540; 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 (CH2Cl2) λmax=432 nm (ε=1897); HRMS (MALDI TOF): m/z [M–] calcd for C72H86: 880.1252; found: 880.1250; 1H NMR (CDCl3): 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); 13C NMR (CDCl3): 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.

Acknowledgements

The author would like to express gratitude Dr. S. Uchida, T. Toya, and T. Nakamura (Nippon Oil Corp.) for device fabrication and measurements. This research is supported in part by NEDO (the New Energy and Industrial Technology Development Organization) and JST, CREST (Japan Science and Technology Agency, Core Research for Evolutional Science and Technology).

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