



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

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ABSTRACT

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-C₆₁-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)-C₆₁-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] (**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.

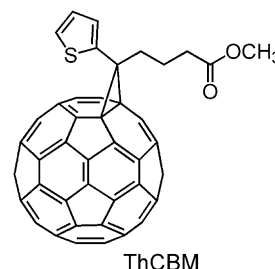
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1. Introduction

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-C₆₁-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



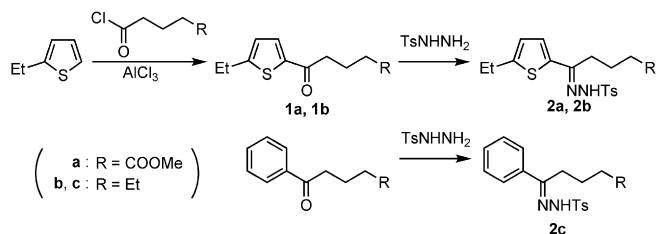
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Recently, Hummelen et al. reported a device fabricated with a thienyl analogue, ThCBM,⁷ for the purpose of improving the miscibility with P3HT. However, there was no clear explanation of the advantages of ThCBM over PCBM. In our previous study, we 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 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-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/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-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 performance of photovoltaic devices that consisted of P3HT and these methanofullerenes.

2. Results and discussion

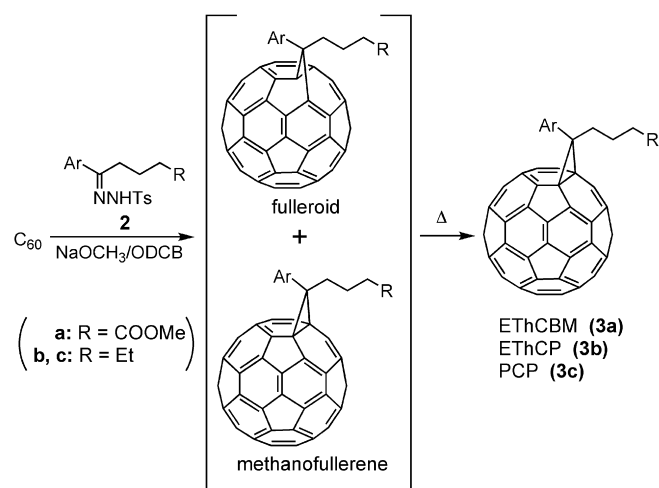
Novel methanofullerenes were synthesized as described in previous papers.⁹ Scheme 1 shows the preparation of tosylhydrazones **2**, the precursors of methanofullerenes. Tosylhydrazones **2a** and **2b** were synthesized by the reaction of *p*-toluenesulfonyl hydrazide (TsNHNH₂) with ketones **1a** and **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.

Methanofullerenes were synthesized 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 R_f 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 R_f 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.

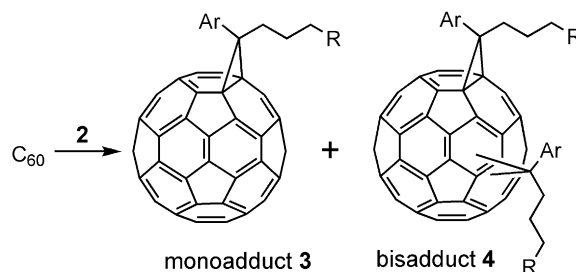
It is well known that the isomers of both [5,6]-fulleroid and [6,6]-methanofullerene are often produced in this reaction, and in



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 ¹³C NMR and the electronic absorption spectra,¹⁰ 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 thienyl substituent.¹¹

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 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 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.^{6d} Solubility data were obtained by the absorption spectroscopic technique because of its higher determination

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