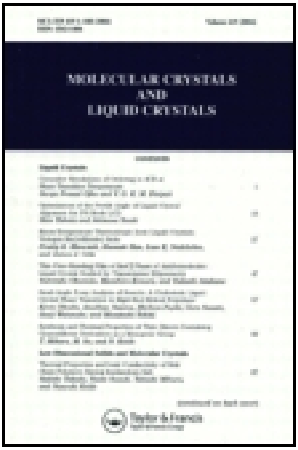

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Mono-Ketone Modified C_{60}s for Acceptor Materials in Organic Photovoltaic Cells

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We designed and synthesized methanofullerene derivatives with several types of thiophenyl mono-*ketone for application in organic photovoltaic cells (OPVCs) as new accepter materials. The various* mono-*ketones having thiophene rings were substituted onto fullerene through application of Hirch-Bingel reaction under mild condition to compete with donor materials especially P3HT [Poly(3-hexylthiophene)] for nano-networking bulk-heterojunction structure where efficient light-induced charge separation is enable by a large-area donor-acceptor interface. The newly synthesized methanofullerene derivatives were characterized through ^{1}H-NMR and FAB Mass spectroscopy. The compounds were also applied in OPV cell devices with P3HT as a donor material and measured electrochemical the property and power conversion efficiency.*

Keywords: acceptor material; fullerene derivatives; n-type semiconductor; organic photovoltaic cells; organic solar cells

INTRODUCTION

Recently, the organic photovoltaic cells (OPVCs) using the mixture of conjugated polymeric materials and donor materials have much attracted due to the feasibility of low cost production and easy manufacturing by solution process [1–2]. Especially, the organic 'bulk heterojunction' structure as an active layer, where efficient light-induced

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charge separation is capable by a large-area donor-acceptor interface [3]. It is known that the achieving high performance in organic solar cell critically depends on increased interface between a conjugated polymer (donor) and a methanofullerene derivative (acceptor), also the formation of networking path for charge transport [4]. Poly(3-hexylthiophene) (P3HT) has widely used as a donor promising material for OPV cells due to the relatively low band gap and high charge carrier mobility. Furthermore, optical and electro property of P3HT can easily controlled by thermal treatment, changing solvent, evaporation conditions. The highest efficiency of OPVCs have been reported around 5% using blends of P3HT and 6,6-Phenyl C_{61} butyric acid methyl ester (PCBM) after thermal annealing process. However, the device performance critically depends on the properties of donor/acceptor materials and the condition of device fabrication [5]. This variability is believed to be influenced on the self-organizing properties of P3HT, which means that both optical and electronic properties are sensitive to the molecular packing. But, the relationship between the molecular properties of the blended materials and the device performance has not been investigated clearly.

In our previous paper, we described the feasibility of newly synthesized 1,3-diketone modified C60s as acceptor materials in OPVCs and this OPVC performed over 3.4% power conversion efficiency under AM 1.5 condition [6]. Here, we are focused on the feasibility of new methanofullerene derivatives with various *mono*-ketones as acceptor materials in OPVCs through Hirch-Bingel reaction which has been known promising method of synthesizing methanofullerene derivative under mild condition.

EXPERIMENTAL

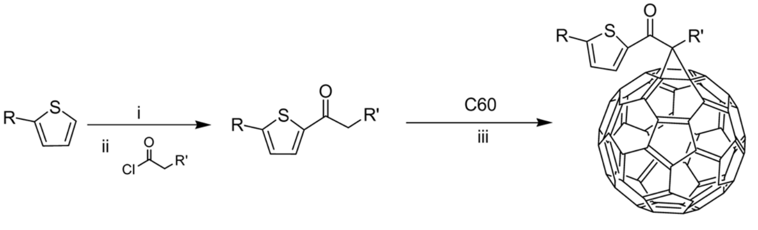
Materials

Thiophene, bithiophene, hexanoyl chloride, octanoyl chloride, *N*-bromosuccinimide (NBS), *n*-butyllithium (2.5 M solution in hexane), magnesium, carbon tetrabromide (CBr_4), 1,8-diazabicylo[5.4.0]undec-7-ene (DBU), and other reagents were purchased from Aldrich Chemicals and used without further purification. P3HT [Poly(3-hexylthiophene)] was purchased from Rieke Metals.

Synthesis of *Mono*-ketone Modified Methanofullerene Derivatives

General Procedure

2-Hexylthiophene, 2-hexyl-5-5′-bithiophene, 1-(thiophen-2-yl)octan-1-one, 1-(2,2′-bithiophen-5-yl)octan-1-one, 1-(5-hexylthiophen-2-yl)hexan-1-one,



1, R = H, R' = *n*-hexyl
2, R = thiophen-2-yl, R' = *n*-hexyl
3, R = *n*-hexyl, R' = *n*-butyl
4, R = 2-hexylthiophen-5-yl, R' = *n*-butyl

SCHEME 1 Synthesis of methanofullerene derivatives containing thiophenyl group. Reaction conditions: (i) NBS, DMF, r.t., 5 h; (ii) Mg, THF, 0 °C, 1 h and r.t., 3 h; (iii) *o*-DCB, CBr_4, DBU, r.t., 2 h.

and 1-(5′-hexyl-2,2′-bithiophen-5-yl)hexan-1-one were synthesized in the similar methods described in the literature [7–8]. Fullerene C_{60} (1.0 mmol) was stirred overnight in *o*-dichlorobenzene solution. And then, 1.2 equiv. of *mono*-ketone and 1.2 equiv. of carbon tetrabromide were added into the reaction mixture. After further stirring for 2 h, 2 equiv. of 1,8-diazabicylo[5.4.0]undec-7-ene (DBU) was slowly added to the reaction mixture. The reaction mixture was kept stirring for 2 h. Products were purified through column chromatography with a mixture of hexane and methylene chloride (3:1 by volume) and recrystallization in hexane to obtain as brown solid.

Synthesis of Compound 1 (Yield: 37%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.41-8.39 (d, $J = 3.0$ Hz, 1H, thiophenyl), 7.84-7.83 (d, $J = 1.5$, 1H, thiophenyl), 7.34-7.31 (t, $J = 3.9$, 1H, thiophenyl), 3.09-3.04 (t, $J = 7.8$, 2H, CH_2), 2.04-1.93 (m, 2H, CH_2), 1.37-1.25 (m, 6H, CH_2), 0.93-0.86 (t, 3H, CH_3) ppm. FAB-MS: 929 (M^+).

Synthesis of Compound 2 (Yield: 35%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.24-8.23 (d, $J = 3.0$ Hz, 1H, thiophenyl), 6.99-6.98 (d, $J = 3.0$ Hz, 1H, thiophenyl), 3.08-3.02 (t, $J = 8.1$ Hz, 2H, CH_2), 2.96-2.87 (t, $J = 12$ Hz, 2H, CH_2), 1.96-1.75 (m, 4H, CH_2), 1.35-1.25 (m,8H, CH_3), 1.04-0.90 (m,6H, CH_3) ppm; FAB-MS: 1011 (M^+).

Synthesis of Compound 3 (Yield: 33%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.31-8.30 (d, $J = 1.5$ Hz, 1H, thiophenyl), 7.44-7.34 (m, 3H, thiophenyl), 7.12-7.09 (t, $J = 3.7$, 1H, thiophenyl), 3.10-3.05 (t, $J = 7.8$, 2H, CH_2), 2.04-1.93 (m, 2H, CH_2), 1.39-1.26 (m, 6H, CH_2), 0.93-0.86 (t,3H, CH_3) ppm; FAB-MS: 984 (M^+).

Synthesis of Compound 4 (Yield: 39%)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 8.29-8.27 (d, $J = 3.0$ Hz, 1H, thiophenyl), 7.25-7.19 (m, 2H, thiophenyl), 6.77-7.76 (d, $J = 1.9$, 1H, thiophenyl), 3.10-3.05 (t, $J = 9.4$, 2H, CH_2), 2.85-2.80 (t, $J = 7.4$, 2H, CH_2), 2.02-1.92 (m, 2H, CH_2), 1.72-1.67 (m, 2H, CH_2), 1.31-1.25(m, 8H, CH_2), 1.05-0.83 (t,6H, CH_3) ppm; FAB-MS: 1067 (M^+).

Device Fabrication

A typical OPVCs in this study contained a layer of polymer thin film between transparent anode (indium tin-oxide, ITO) and a LiF/Al cathode. The active polymeric material was a mixture of each new methanofullerene as an acceptor material and P3HT as a donor material. To fabricate the organic photovoltaic cells, the patterned ITO glass substrates were cleaned by ultrasonic treatment in detergent, deionized water, acetone, and isopropyl alcohol, sequentially. After treatment of UV/ozone on the surface of ITO, PEDOT-PSS (Bytron, Al 4083) was casted by spin-coating a thin layer (about 40 nm). Post thermal treatment was followed on the substrates at 200°C for 5 min. And then, solutions of P3HT blended with each new methanofullerenes were spin-coated from *o*-dichlorobenzene (*o*-DCB) solution on the PEDOT-PSS layer. Finally, the cathode consisting of LiF and Al layer was thermally deposited on top of the active layer under vacuum of 10^{-7} torr. The active area size of device was measured around 0.04 cm^2.

Instruments

^{1}H-NMR spectra were obtained on Bruker DPX-300 spectrometer at 300 MHz. Cyclic votametry was measured in solution state on Bas 100B electrochemical analyzer at room temperature. UV-Vis absorption spectra of each compound were taken by Shimadzu UV-2550 spectrophotometer. Photocurrent-voltage curve was measured by Keithley 2400 under AM 1.5 simulated light (ORIEL 300 W Xenon lamp). The light intensity (100 mA/cm^2) of the illumination source was confirmed by using a standard silicon photodiode (BS520, Bunkoh-Keiki).

RESULTS AND DISCUSSION

Design and Synthesis of Methanofullerene Derivatives with Various Ketones

To improve the solubility of fullerene and enhance the electron affinity, we have designed methanofullerene derivatives with various ketones. In addition, we incorporated thiophenyl and bithiophenyl groups to increase the compatibility with conventional donor polymer, such as P3HT. The *mono*-ketone compounds having thiophenyl group were easily synthesized from the method in the literature [7–8]. Compound **1**, **2**, **3**, and **4** were produced as similar procedure at literature through Hirch-Bingel reaction under mild condition [9–10]. Fullerene C_{60} (1.0 mmol) was reacted with slightly excess of ketones in the presence of carbon tetrabromide and 2 equiv. of 1,8-diazabicylo[5.4.0]undec-7-ene (DBU). After work-up, major products can be purified by column chromatography with the mixture of hexane and methylene chloride as an eluent. Compound **1**, **2**, **3**, and **4** can be obtained as yield of 35%, 37%, 33%, and 39%, respectively.

The molecular structure of each compound was characterized by ^{1}H NMR and the FAB (fast atom bombardment) mass spectroscopy. Also, we can confirm that all of these compounds have good solubility in common solvent, such as, *o*-dichlorobenzene, *mono*-chlorobenzene, chloroform, and methylene chloride.

Photophysical and Electrochemical Properties of Methanofullerene Derivatives with Various Ketones

We have performed the UV absorption experiments. Figure 1 shows the UV-Visible absorption of each compound in methylene chloride solution. Each compounds feature two major absorption peaks at 480 and 500 nm, and one small peak at 700 nm (Figure 2). Compound **2** and **4** show red-shifted absorption peaks compare to compound **1** and **3** by several nm. This means that bithiophenyl group of compound **2** and **4** is much more effective electron acceptor than thiophenyl group of compound **1** and **3**. From this result, we can control the bandgap of methanofullerene by verifying the attached moiety on the fullerene molecules.

Each Compound shows slightly different cyclic voltammograms with three distinctive quasireversible reduction waves in the potential ranging from 0.0 V to −2.0 V. To get clear and distinguished curves, we choose tree representative curves in Figure 3 and more detailed data were listed in Table 1. As a result of this experiment, we could make result that compound **2** and **4** having bithiophenyl group showed much lower reversible reductive potentials in comparison to compound

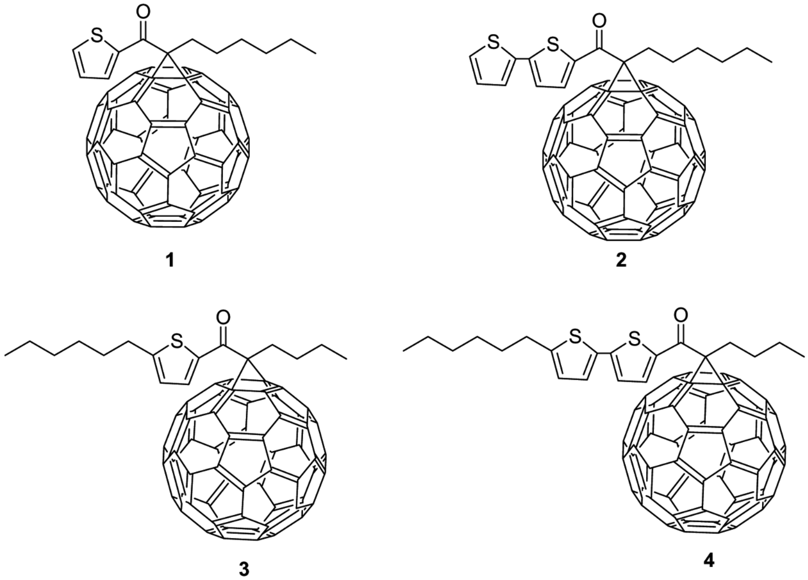


FIGURE 1 Structure of *mono*-ketone modified C60s.

1 and **3** by 0.02 V. This means the LUMO energy levels of compound **2** and **4** are slightly lower than those of compound **1** and **3**, that is to say, LUMO level of bithiophene substituted compounds (**2** and **4**) is lowered by increasing electron density. We believe that the more fluent

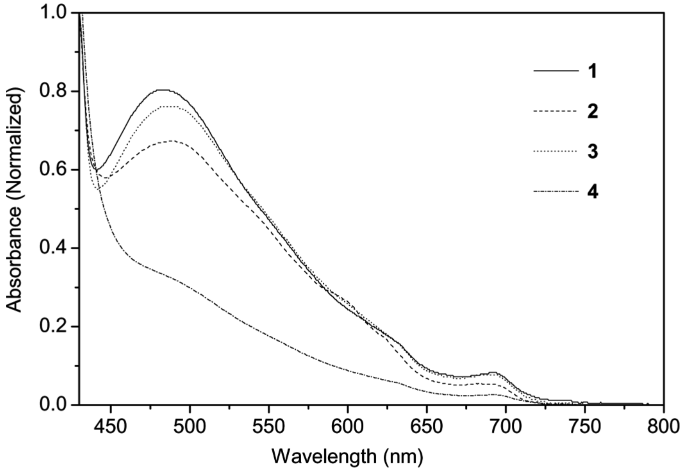


FIGURE 2 UV Absorption Spectra of Compound **1**, **2**, **3**, and **4**.

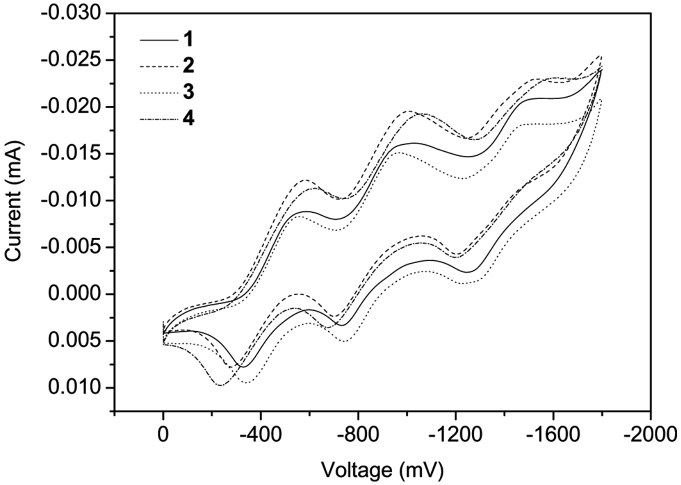


FIGURE 3 Cyclic voltamograms of compound **1**, **2**, **3**, and **4**.

electrons of substituent on fullerene can make the lower LUMO level, the electron of bithiophenyl group is much richer than that of thiophenyl. We confirmed the relation of the LUMO level by Cyclic Voltammetry experiment.

The Performances of Organic Photovoltaic Cells

We fabricated the organic photovoltaic cells using a mixture of P3HT and one of newly synthesized methanofullerene derivatives. The *J-V* characteristics of OPVCs are shown in Figures 4–5 and other performances are summarized in Table 2. As shown in Figure 5, OPVCs using compound **1–4** as acceptor material show good diode behavior at the range of −0.5 and −0.4 V in the dark conditions. In addition, current density of each device under dark is very low value about

TABLE 1 Electrochemical Properties and Energy Levels of Compound **1**, **2**, **3**, and **4**

Compound	$E^1_{\rm red}$(V)	$E^2_{\rm red}$ (V)	$E^3_{\rm red}$(V)	LUMO (eV)*
1	−0.45	−0.86	−1.37	−4.18
2	−0.43	−0.85	−1.36	−4.16
3	−0.44	−0.85	−1.36	−4.17
4	−0.42	−0.86	−1.39	−4.15

*LUMO energy level of PCBM was used as reference as − 4.2 eV.

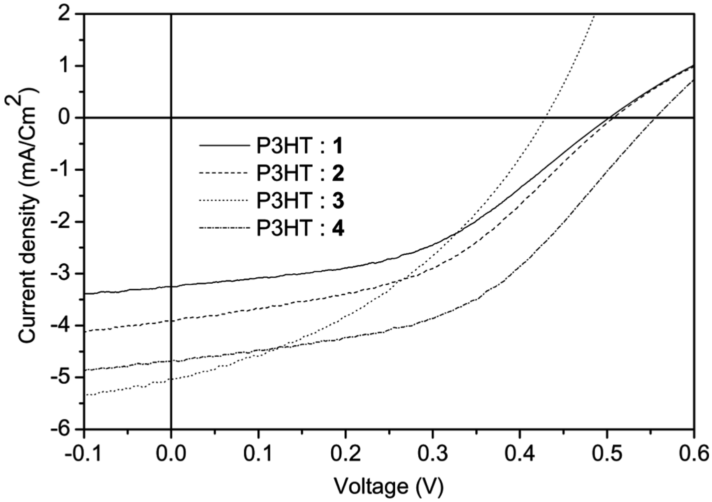


FIGURE 4 *J-V* characteristics of ITO/PEDOT: PSS/P3HT: *Mono*-ketone modified methanofullerene/LiF/Al heterojunction at pristine condition.

10^{-6} mA/cm^2. This low leakage current value proves that the interfacial resistance of our OPVCs is very low and device fabrication skill is not bad to realize reasonable OPVC.

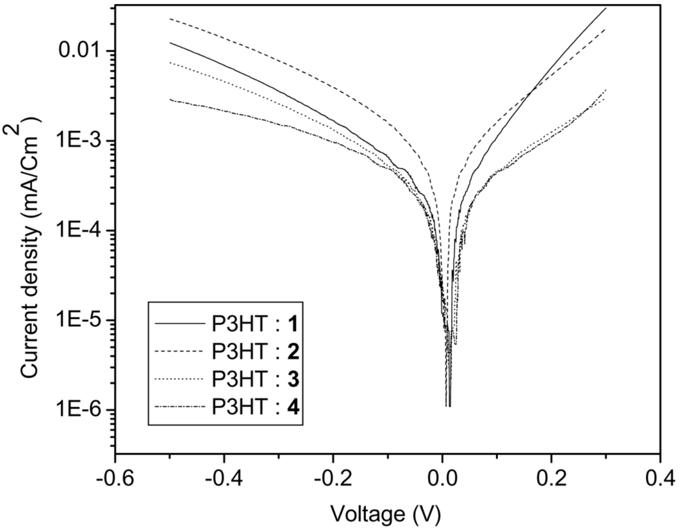


FIGURE 5 *J-V* characteristics of ITO/PEDOT: PSS/P3HT: Compound/LiF/Al after annealing at 170°C for 5 min in a logarithmic scale.

TABLE 2 Photovoltaic Properties of OPVC at Pristine Condition Using one of Compound **1**, **2**, **3**, and **4** as Acceptor Materials

	P3HT:1	P3HT:2	P3HT:3	P3HT:4
Voc (mV)	502	505	429	555
Jsc (mA/Cm^2)	3.2	3.9	5.0	4.7
FF (%)	45	44	38	47
PCE (%)	0.73	0.87	0.84	1.27

*Under AM 1.5 simulated light illumination (100 mW/cm^2).

The device performances were measured under pristine condition, that is to say, without thermal treatment. Power conversion efficiency of each device is recorded from 0.73% to 1.27%. Devices using compound **2** or **4** as acceptor materials show better performance than those using compound **1** or **3** as acceptor materials. As you can see in the previous Cyclic Voltammetry experiment, we have already confirmed that bithiophenyl group has much higher electron attraction ability than mono-thiophenyl group when they are attached at fullerene C60s. Now, we can conclude that the number of substituted thiophene rings is proportionate in the electron affinity of methanofullerene.

In conclusion, we are designed and synthesized four kinds of *mono*-ketone modified fullerenes (compound **1**, **2**, **3**, and **4**) having thiophenyl or bithiophenyl substituent. And OPVCs using these compounds as acceptor materials with P3HT donor shows moderate power conversion efficiency around 1% under AM 1.5 simulated light illumination. Especially, compound **4** shows highest efficiency as 1.27% under pristine condition. Compound **4** has the highest solubility and lowest LUMO level among newly synthesized methanofullerene derivatives in this paper. High solubility and low LUMO level of compound **4** can affect to modify the donor-acceptor bulk-heterojunction and improve electron attraction ability from P3HT donor. Consequently, we can confirm that solubility and electron affinity of acceptor molecules are very important factors to increase power conversion efficiency in OPVCs and we are studying on the improvement of photovoltaic performance using compound **4**.

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