



Synthesis and characterization of new acetalized [60]fullerenes

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ABSTRACT

Acetalized [60]fullerenes were synthesized from cyclohexanone-fused [60]fullerene, which was facilely prepared by Diels–Alder reaction of C_{60} with silyl ether diene, on treatment of various aliphatic alcohols under $TiCl_4$ catalyst. The spiro-cyclic acetalized [60]fullerenes having five, six, and seven-membered rings were also synthesized by using the corresponding diols under the same condition. The slightly raised reduction potentials E^{red} (~ 0.04 V) relative to those of PCBM were observed by cyclic voltammetry measurement, depending on the identity of alkyl group/chain. The noncyclic acetalized [60]fullerenes showed lower thermal stability up to 200 °C, while the cyclic ones exhibited the drastically improved thermal stability up to 350 °C under nitrogen atmosphere. The acid-catalyzed hydrolysis easily removed the acetal moiety quantitatively, resulting in a considerable change of solvent solubility of the fullerene.

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Chemically functionalized fullerenes have recently attracted much attention as n-type semiconductor materials owing to their slightly raised LUMO energy level relative to the pristine C_{60} and the improved solubility required both for wet processing to fabricate thin film and for co-mixing with p-type materials represented by P3HT.¹ The most widely used n-type fullerene derivative is [6,6]-phenyl- C_{61} -butyric acid methyl ester, PCBM, and many researches have been devoted to properly raise the LUMO level by minor² or major (e.g., SIMEF and ICBA)³ modifications to increase the open-circuit voltage and the resulting power conversion efficiency on organic thin-film solar cells.

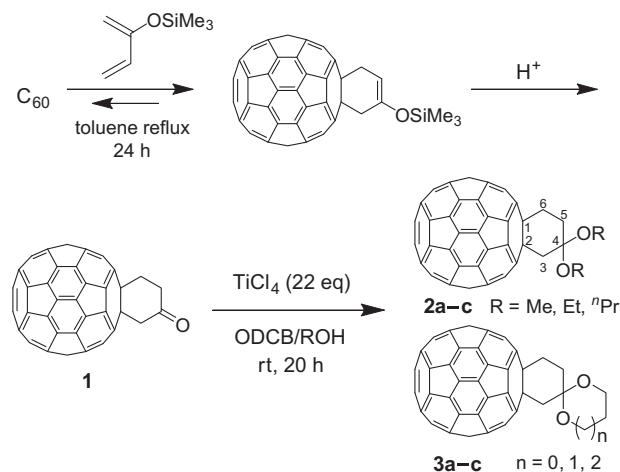
To develop versatile synthetic methods for a series of requisite derivatives, a key precursor fullerene is desired to fulfill some intrinsic properties such as facile accessibility with high mono-adduct selectivity, easy purification, further modifiability, and sufficient stability. One of the most promising candidates to be applicable is cyclohexanone-fused fullerene **1**⁴ which has a less congested carbonyl group capable of being converted into some functional groups, such as alcohol/ester^{4,5} and imine/amine.⁶ However, the introduction of other possible groups to **1** including acetal group has not been reported yet.

Acetal group can be introduced by a simple nucleophilic attack of alcohols to a carbonyl group of **1** and thus various alcohols can be employed to tune its electronic properties desired as n-type materials. Moreover, the acetal group can be deprotected by simple hydrolysis with an acid catalyst in order to change the solvent solubility. Such control of fullerene solubility could be very useful in multi-layered wet fabrication process⁷ as well as in

nanolithography.⁸ However, only a few examples of acetalized fullerene have been hitherto synthesized incidentally.⁹

Herein we report a facile synthesis of new acetalized [60]fullerenes **2** and **3** by $TiCl_4$ -mediated reaction of cyclohexanone-fused fullerene **1** with several alcohols. Their electronic properties as well as the thermal stability seem to make them as a new candidate for n-type materials.

The Diels–Alder reaction of C_{60} with a slight excess of 2-trimethylsilyloxy-1,3-butadiene (1.1 equiv) was carried out in toluene at reflux temperature for 24 h by a previously reported method⁴ (Scheme 1). The resulting [2+4] adduct was readily



Scheme 1. Synthesis of acetalized fullerenes **2** and **3** by the reaction of cyclohexanone-fused **1** with various alcohols and diols.

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Table 1
TiCl₄-mediated acetalization of cyclohexanone-fused **1** with various alcohols^a

2/3	Alcohol	Temp. (°C)	Conv ^b (%)	Yield ^{b,c} (%)	Isolated yield (%)
2a	MeOH	rt	67	>99	61
2b	EtOH	rt	40	>99	36
2c	1-PrOH	rt	28	>99	27
–	2-PrOH	50	tr ^d	–	–
3a^e	HO(CH ₂) ₂ OH	rt	80	>99	73
3b^e	HO(CH ₂) ₃ OH	rt	93	>99	65
3c^e	HO(CH ₂) ₄ OH	rt	52	>99	35

^a The reaction of **1** (100 mg) with alcohol (6 mL) was carried out in the presence of TiCl₄ (300 μL, 22 equiv) in ODCB (20 mL) for 20 h.

^b Determined by HPLC.

^c Based on C₆₀ consumed.

^d Trace amount.

^e In ODCB/THF/alcohol (10/10/2 in mL).

decomposed on silica gel column chromatography to afford cyclohexanone-fused fullerene **1** in good yield (65%). In general, Diels–Alder [2+4] adduct of C₆₀ is likely to undergo retro-reaction. However, the present Diels–Alder reaction is designed to avoid the retro-reaction by the following facile desilylation, giving the thermally stable monoadduct **1**. The bisadducts were also detected by HPLC using a Buckyprep column (~15%) as a mixture of the isomers.

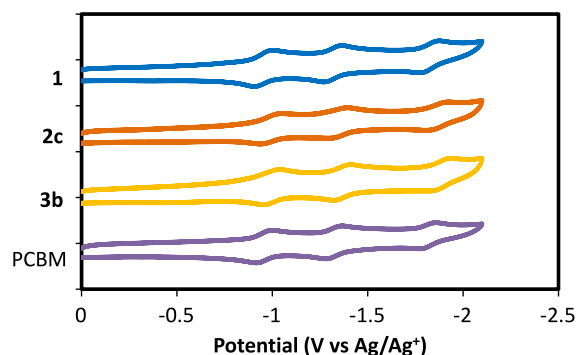
The reactions of **1** with various alcohols in the presence of TiCl₄ (ca. 20 equiv) were carried out in *o*-dichlorobenzene (ODCB)/alcohol (20/6 by v/v) at room temperature for 20 h by modification of the reported method¹⁰ (Table 1). Tracing with HPLC, the reaction was quenched by the addition of triethylamine (500 μL) and acetals **2/3** were isolated by silica gel column chromatography (CS₂/ethyl acetate = 9/1 for **2a**; CS₂/diethyl ether = 94/6 for **3b**; toluene for others). The conversion for **2a–c** decreased in the order of alcohol alkyl groups Me **2a** < Et **2b** < Pr **2c** due to the increased steric bulk. The secondary alcohol 2-PrOH was hardly reacted due to the unendurable steric hindrance. The diols HOCH₂CH₂(CH₂)_nOH (*n* = 0–2) were reacted with **1** to give a good to fair amount of the spiro-cyclic acetals **3a–c** by using a mixed-solvent of ODCB/THF (10/10 by v/v) in order to improve the mixability of diols to ODCB. Because acetalization is a reversible reaction, all alcohols and solvents used were dried and distilled before use. Nevertheless, a stoichiometric amount of TiCl₄ was needed for the satisfied conversion due to its deactivation by the stoichiometrically formed water. Some unidentified byproducts, probably the hemiacetals and the noncyclic acetal, were also formed when we used ethylene glycol as purchased.

The structures of **2/3** were determined by ¹H and ¹³C NMR analysis and MALDI-TOF-MS spectroscopy.¹¹ The ¹H NMR spectrum of **2a** (in CS₂/CDCl₃) showed two sets of ddd (observed as multiplet) protons at 3.05 and 3.50 ppm (both 2H), which were assigned to the cyclohexyl methylene protons on C5 and C6 carbons, respectively. Other two singlet protons at 3.53 (6H) and 3.74 (2H) ppm were assigned to methoxy and isolated methylene (C3) protons. Such a large down-field shift for C6- and C3-methylene protons is clearly due to the strong electron-withdrawing effect of the fullereryl moiety as well as the acetal moiety. The sharp peak for these singlet protons indicates that the cyclohexane ring is somewhat flexible to flip in the time scale of NMR at room temperature. The ¹³C NMR of **2a** showed 7 aliphatic sp³ signals including an acetalic carbon (101.96 ppm) and 28 signals in sp² fullerene region indicating C₅ symmetry of the fullereryl moiety. The high resolution MALDI-TOF-MS exhibited the molecular ion peak at 836 *m/z* in negative mode. The ¹H NMR spectra of **2b** and **2c** showed similar characteristics to those of **2a**, while the α-methylene protons in each alkoxy group showed a slightly different chemical shift due to the difference in axial/equatorial positions. The cyclic acetals

3a–c also showed essentially the same ¹³C signal patterns to **2a** with an acetalic carbon peak at around 100 ppm and 28 sp² fullereryl signals.

To elucidate the electronic property of acetalized fullerenes, the reduction potentials of **1**, **2c**, and **3b**, and PCBM were measured by cyclic voltammetry using Ag/AgCl reference electrode and Pt as both working and counter electrode in ODCB (Fig. 1). All cyclic voltammograms showed clear three pairs of reversible peaks in reduction region. The first reduction potential *E*₁ (V vs Fc/Fc⁺) of ketone **1** was the same as that of PCBM (–1.17) (Table 2). However, those of compounds **2** and **3** (–1.21) were slightly shifted to negative potential up to 0.03–0.04 V due to the electron-donating ability of the alkoxy substituent as compared with those of **1** and PCBM. The slightly raised LUMO level has been reported to be effective to increase the open-circuit voltage *V*_{OC}, which is a key factor on power conversion efficiency (PCE) in an organic thin layer solar cell.¹³ The slightly higher LUMO level of acetals **2/3** would be expected to exhibit the larger *V*_{OC} than that of PCBM in the combination of P3HT.

Considering that acetal C–O bond seems to be easily degraded as compared to the simple ether bond, the thermal stabilities of **2** and **3** were measured by thermogravimetric analysis under nitrogen atmosphere (Fig. 2). The noncyclic acetal **2a** showed a rather lower decomposition temperature at 200 °C, while cyclic acetals **3** exhibited the excellent stability up to 350 °C for **3a**, 320 °C for **3b**, and 270 °C for **3c**. The gradual weight loss for **3** from 150 °C as compared with that of **2a** is probably due to the residual solvent or diol, because we confirmed no change of the sample after heating up to 280 °C under nitrogen by HPLC analysis. The weight loss of **3** up to this temperature is less than 2 wt% and does not correspond to the wt% of diol moiety (5.3–8.4 wt% for **3a–c**). In

**Figure 1.** Cyclic voltammograms of fullerene derivatives **1**, **2c**, **3b** and PCBM in ODCB.**Table 2**
Reduction potentials of fullerenes **1–3** and PCBM in ODCB

	<i>E</i> ^{red} V versus Fc/Fc ⁺ ^a			LUMO ^b (eV)
	<i>E</i> ₁	<i>E</i> ₂	<i>E</i> ₃	
C ₆₀	–1.09	–1.47	–1.92	–3.71
1	–1.17	–1.53	–2.04	–3.63
2a	–1.20	–1.57	–2.11	–3.60
2b	–1.21	–1.57	–2.11	–3.59
2c	–1.21	–1.56	–2.11	–3.59
3b	–1.21	–1.58	–2.12	–3.59
PCBM	–1.17	–1.54	–2.03	–3.63

^a Reduction potentials *E*_{red} = 0.5 (*E*_p^{ox} + *E*_p^{red}) were measured versus Ag/AgCl reference electrode and standardized to Fc/Fc⁺ couple *E*_{Fc/Fc⁺} = +0.215 V versus Ag/Ag⁺ (ODCB)] in 0.1 mM ODCB with 0.1 M ⁿBu₄PF₆ as supporting electrolyte. Scan rate was 100 mV/s.

^b Calculated from *E*₁ using LUMO level = –*e* (*E*₁^{red} + 4.8).¹²

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