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$FeCl_3$-Mediated Synthesis of Fullerenyl Esters as Low-LUMO Acceptors for Organic Photovoltaic Devices

Masahiko Hashiguchi,[*,†] Naoki Obata,[‡,§] Masashi Maruyama,[‡] Kee Sheng Yeo,[‡] Takao Ueno,[†] Tomohiko Ikebe,[†] Isao Takahashi,[†] and Yutaka Matsuo[*,‡]

Fullerene Development Group, Performance Products Division, Mitsubishi Chemical Corporation, 1-1 Kurosakishiroishi, Yahatanishi-ku, Kitakyushu 806-0004, Japan, Department of Chemistry, The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan, and Mitsubishi Chemical Group Science and Technology Research Center, Inc., 1000 Kamoshida, Aoba-ku, Yokohama, Kanagawa, 227-8502, Japan

6206530@cc.m-kagaku.co.jp; matsuo@chem.s.u-tokyo.ac.jp

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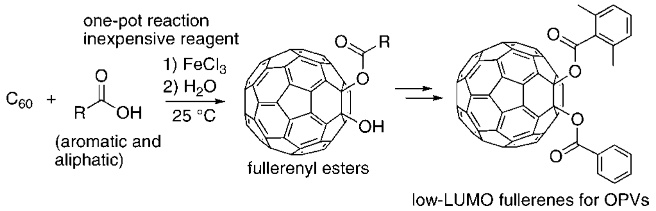
ABSTRACT



C_{60} reacted with aromatic and aliphatic carboxylic acids in the presence of inexpensive $FeCl_3$ at room temperature to produce hydroxyfullerenyl esters $C_{60}(OCOR)(OH)$ in up to 68% isolated yield. The hydroxyl group was utilized in functional group transformations to obtain a diester derivative $C_{60}(OCOAr)(OCOPh)$ (Ar = 2,6-xylyl) and a siloxyl derivative $C_{60}(OCOAr)(OSiMe_3)$. The diester and siloxyl derivatives were found to possess low-lying LUMO levels were utilized in organic photovoltaic devices showing 1.3% power conversion efficiency.

Development of fullerene derivatives having various LUMO levels is important for organic photovoltaic (OPV) applications.[1] Although obtaining high-LUMO fullerenes is relatively straightforward, since the addition of carbon functional groups to fullerene generally raises LUMO levels,[2] the approach toward low-LUMO fullerenes is rather limited.[3]

Fullerenyl esters[4] are considered to be suitable for OPV application as low-LUMO acceptors: these compounds bear electron-withdrawing ester moieties and exhibit high solubility in organic solvents. For fullerenyl esters, only the synthesis of acetoxylated fullerenes and C_{60}-fused lactones have been reported in the literature.[4,5] These compounds have

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[†] Fullerene Development Group, Performance Products Division, Mitsubishi Chemical Corporation.

[‡] Department of Chemistry, The University of Tokyo.

[§] Mitsubishi Chemical Group Science and Technology Research Center, Inc.

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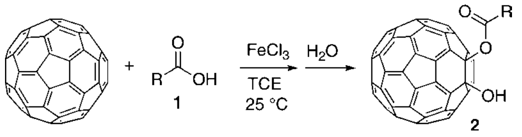
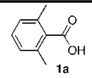
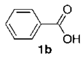
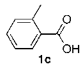
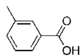
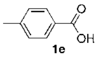
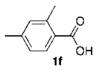
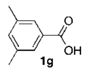
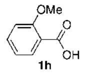
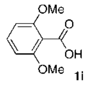
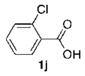
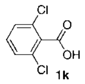
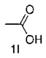
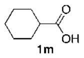
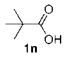
Table 1. Reaction Conditions and Yields for the Reaction of C_{60} with Carboxylic Acids **1a**–**n** in the Presence of $FeCl_3$[a]



carboxylic acids **1**	reaction time (hour)	conversion of C_{60} (%)[b]	HPLC area ratio (%)[b]	yields of **2** (%)[c]
 1a	4	95	79	68
 1b	8	95	49	14
 1c	8	96	49	28
 1d	7	95	49	25
 1e	7	96	51	24
 1f	8	97	56	30
 1g	8	96	44	22
 1h	8	–	–	–[d]
 1i	8	–	–	–[d]
 1j	5	91	54	35
 1k	8	–	–	–[d]
 1l	4	90	64	29
 1m	6	76	54	21
 1n	8	52	32	10

[a] All reactions were performed under a nitrogen atmosphere with a molar ratio of C_{60}/$FeCl_3$/**1** = 1:20:10. [b] Conversion of C_{60} and selectivity of product were determined by HPLC analysis. [c] Isolated yield. [d] No reaction.

been synthesized through one-pot reactions with (diacetoxy)iodobenzene,[4a] $Mn(OAc)\cdot 2H_2O$, or $Pb(OAc)_4$.[4c−e] However, a general synthetic methodology to obtain fullerenyl esters with a broad substrate scope has not been realized so far.

Herein we report facile one-pot syntheses of hydroxyfullerenyl esters $C_{60}(OCOR)(OH)$ by using versatile carboxylic acids and inexpensive iron trichloride ($FeCl_3$). This reaction proceeds under mild conditions and possesses substrate diversity catering to both aromatic and aliphatic carboxylic acids.

Treatment of C_{60} with 2,6-dimethylbenzoic acid (**1a**, 10 equiv) in the presence of $FeCl_3$ (20 equiv) in 1,1,2,2-tetrachloroethane (TCE) at 25 °C for 4 h produced 1-hydroxy-2-{2,6-dimethylphenylcarbonyloxy}[60]fullerene (hydroxylfullerenyl 2,6-dimethylbenzoate), $C_{60}(OCOC_6H_3Me_2\text{-}2,6)$ (**2a**), in 68% isolated yield (Table 1, entry 1). Aromatic organic solvents such as toluene and xylene, often used in the synthesis of fullerene derivatives, were found to be unsuitable for this reaction. The use of toluene and xylene causes a side reaction, hydroarylation,[6] which is mediated by Lewis acidic $FeCl_3$. This will in turn lead to a decrease in the chemical yield of the desired product. Therefore, TCE was chosen instead as the solvent for this reaction, since it did not have any aromatic component, and it could dissolve the starting material C_{60}. This reaction afforded almost quantitative conversion of C_{60} upon stirring at rt for 4–8 h. As shown in Table 1, **2a** was obtained as the main product. Possible side products in this reaction were di- and multiadducts. Although numerous side products were formed due to the inevitable formation of regiochemical isomers of di- and multiadducts, the absolute amount obtained for each side product was very small. The drawback of this reaction was the need for a large excess of substrates and $FeCl_3$; maximum selectivity was obtained when 10 equiv of carboxylic acid and 20 equiv of $FeCl_3$ were used (Table S4). Nevertheless, this reaction is highly applicable to industrial production because of the relative low cost of both substrate and iron trichloride as compared to C_{60}. The reaction mechanism is still unclear, but we propose that the mechanism involves a cationic fullerene as a key intermediate (Scheme S1).[6d]

Product **2a** can be purified with either silica-gel column chromatography or HPLC separation. Purified compound **2a** was characterized with ^1H and ^{13}C NMR, IR, electrospray ionization (ESI)-mass spectroscopic analysis, and elemental analysis. The structure of **2a** was determined unambiguously by X-ray crystallographic analysis of its single crystal, which was obtained by slow evaporation of a CS_2 solution of **2a** (Figure 1). It was elucidated from the X-ray structure that the arylcarbonyloxyl group and the hydroxyl group were added to C_{60} in a 1,2-addition pattern.

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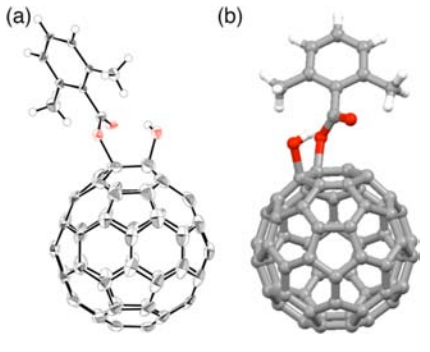


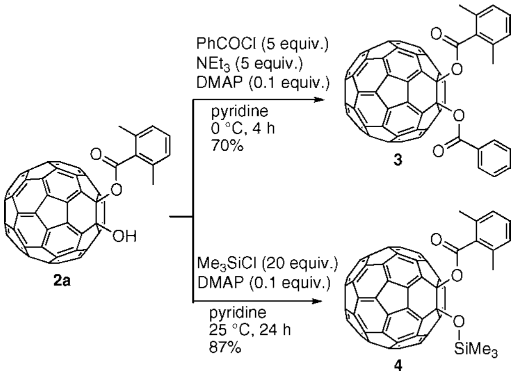
Figure 1. Crystal structure of **2a**·$0.5CS_2$. (a) ORTEP drawing with thermal ellipsoids at 30% probability. (b) Ball-and-stick model.

The scope and limitation of the reaction is illustrated in Table 1. The reaction was applicable to both aromatic and aliphatic carboxylic acids, though the latter type gave lower yields. Nonsubstituted benzoic acid (**1b**) showed similar reactivity to **1a** (conversion of C_{60} = 95%), but comparatively low selectivity, to produce the corresponding fullerenyl ester **2b** (14% yield, entry 2). We postulate that the poor selectivity was caused by the coordination of $FeCl_3$ to the carbonyl group of the substrate. Another potential reason for this low yield would be the side reaction between a possible cationic fullerene intermediate (vide infra) and nonsubstituted aryl groups. There had been many reports on reactions of fullerene cations with aryl groups in literature.[5c,6a,6d,7] Monomethylated benzoic acids **1c**, **1d**, **1e**, gave corresponding fullerenyl esters **2c**, **2d**, **2e**, in chemical yields of 24−28%. For dimethylated benzoic acids, 2,4-dimethylbenzoic acid (**1f**) afforded a 30% yielding reaction, while 3,5-dimethylbenzoic acid (**1g**) gave a comparatively lower yield of 22%. 2-Methoxybenzoic acid (**1h**) and 2,6-dimethoxybenzoic acid (**1i**) did not produce any fullerenyl ester, most likely due to coordination of $FeCl_3$ to the methoxy groups. 2-Chlorobenzoic acid (**1j**) gave the second best result (35% yield), but 2,6-dichlorobenzoic acid (**1k**) did not yield any fullerenyl ester at all. Aliphatic carboxylic acids **1l**, **1m**, **1n** reacted with C_{60} under the same conditions to produce fullerenyl esters **2l**, **2m**, **2n**, respectively. Among these three substrates, pivalic acid (**1n**) gave the lowest yield. The reason for this result is unclear, but we consider the electronic nature of the substrates also affects the yield.

Attempts to use aldehydes such as benzaldehyde and esters such as ethyl benzoate, in place of carboxylic acids, were unsuccessful when similar reaction conditions were used. Wang et al. had previously reported an $Fe(ClO_4)_3$-mediated addition of aldehydes and esters to fullerene.[8] We attempted the reaction using other Lewis acids, oxidants, and iron complexes ($AlCl_3$, $RuCl_3$, $BF_3 \cdot Et_2O$, $CuCl_2$, $FeCl_2$, $ZnCl_2$, $Fe(acac)_3$, and $Fe(ClO_4)_3$) in place of $FeCl_3$, but we also could not obtain the desired fullerenyl esters from their respective carboxylic acids. Therefore, this reaction was found to be specific for $FeCl_3$ and carboxylic acids only.

Next, we performed functional group transformations on the hydroxyl groups of **2a**. Electrochemical studies of **2a** showed its irreversible reduction/oxidation process due to the presence of the hydroxyl group. Masking the hydrogen atom of the hydroxyl group is thus necessary to obtain an electrochemically stable fullerene-based electron acceptor for application in OPV devices. Syntheses of fullerene ethers and esters from fullerenols is generally straightforward.[5b] Treatment of fullerenol **2a** with benzoic acid chloride (5 equiv), in the presence of diethyl amine (5 equiv) and dimethylaminopyridine (DMAP, 0.1 equiv) in pyridine at 0 °C for 4 h, produced a diester derivative **3** in 70% yield (Scheme 1). A siloxyl derivative **4** was also obtained in 87% yield via the reaction of fullerenol **2a** with trimethylsilyl chloride (20 equiv), in the presence of DMAP (0.1 equiv) in pyridine at 25 °C for 24 h. Compounds **3** and **4** were characterized via ^1H NMR, ^{13}C NMR, IR, ESI-MS, elemental analysis, and X-ray crystallography.

Scheme 1. Synthesis of Compounds **3** and **4**



Electrochemical studies were performed on **3** and **4** to determine the LUMO levels of the compounds (Table 2). Both compounds **3** and **4** exhibited reversible reductive waves, as observed in the measurements. The first reduction potential for both **3** and **4** in 1,2-dichlorobenzene was −1.11 and −1.13 V vs Fc/Fc^+. The LUMO level of **3** was formally calculated to be −3.69 eV. This value is the same as that for the LUMO level of C_{60} (−3.69 eV, estimated

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from electrochemical measurement in 1,2-dichlorobenzene) but lower than that of PCBM (−3.61 eV). The two electron-withdrawing groups attached to each fullerene molecule confer large electron affinities and low LUMO levels to products **3** and **4**. These compounds are considered to be rare; they possess low-LUMO levels similar to C_{60}, while at the same time they exhibit a much higher solubility than C_{60}. DFT calculation (B3LYP/6-311+G** level, Supporting Information) revealed that the LUMO of **3** and **4** are localized on the fullerene core, not on the carbonyl groups.

Table 2. Reduction Potentials and LUMO Levels for **3** and **4** in Comparison with C_{60} and PCBM[a]

	$E_{1/2}^{\mathrm{red}}$ (V vs Fc/Fc$^+$)			
compd	E_1	E_2	E_3	LUMO level (eV)[b]
C_{60}	−1.11	−1.49	−1.93	−3.69
3	−1.11	−1.49	−1.93	−3.69
4	−1.13	−1.50	−1.94	−3.67
PCBM	−1.19	−1.56	−2.05	−3.61

[a] Potentials in V vs a ferrocene/ferrocenium (Fc/Fc$^+$) couple were measured by cyclic voltammetry in a 1,2-$Cl_2C_6H_4$ solution containing $Bu_4N^+PF_6^-$ as a supporting electrolyte at 25 °C with a scan rate of 0.1 V s^{-1}. Glassy carbon, platinum wire, and Ag/Ag$^+$ electrodes were used as the working, counter, and reference electrodes, respectively. [b] Estimated using the following equation: LUMO level = $-(4.8 + E_{1/2}^{\mathrm{red1}})$ eV.[9]

Compounds **3** and **4** were both examined for suitability in OPV application, via the fabrication of bulk heterojunction solar cells with poly(3-hexylthiophene) (P3HT) or poly(4,8-bis-octoxybenzo(1,2-*b*:4,5-*b*)dithiophene-2,6-diyl-alt-(dodecyl-thieno(3,4-*b*)thiophene-2-carboxylate)-2,6-diyl) (PBDTTT)[10] as the donor material in the active layer. We summarized the device performances in Table 3. Device 1 showed respectable performance with an open-circuit voltage (V_{OC}) of 0.74 V, a short-circuit current density (J_{SC}) of 5.4 mA/cm^2, and a fill factor (FF) of 0.34. Although the power conversion efficiency (PCE, 1.3%) was lower than that of standard OPV devices,[2e] the results contained valuable information. The low-lying LUMO (−3.55 eV) and HOMO (−5.12 eV) levels of the low band-gap polymer, PBDTTT, are compatible with the low-lying LUMO levels of compounds **3** and **4**. This results in a higher V_{OC} as compared to when using P3HT. Also, PBDTTT absorbs in the near-IR region of the solar spectrum, contributing to the higher J_{SC} seen in devices 1 and 2. Due to the recent push toward using low band-gap polymers as electron-donating materials in OPVs, electron-accepting materials with low-lying LUMO levels, such as compounds **3** and **4**, are expected to serve as diverse materials in the photovoltaic research field, playing a strategic role in the future enhancement of OPV performance.

Table 3. OPV Device Performance for Compounds **3** and **4**[a]

device	compd	donor	V_{OC} (V)	J_{SC} (mA/cm^2)	FF	PCE (%)
1	**4**	PBDTTT	0.74	5.4	0.34	1.3
2	**3**	PBDTTT	0.69	5.0	0.32	1.1
3	**4**	P3HT	0.46	2.2	0.39	0.40
4	**3**	P3HT	0.46	2.1	0.29	0.28

[a] Information for the device configurations are stored in the Supporting Information.

In summary, we have demonstrated a facile synthetic methodology to introduce two electron-withdrawing groups to fullerene, to obtain fullerene electron acceptors that have low LUMO levels. The synthesis relies on $FeCl_3$-mediated introduction of carbonyloxyl groups by using carboxylic acids. Inexpensive $FeCl_3$ is used for this reaction, and the reaction proceeds under mild conditions. Although there are some limitations on the carboxylic acid substrates due to the use of Lewis acidic $FeCl_3$, it has been observed that both aromatic and aliphatic carboxylic acids are compatible with this reaction. Fullerenyl esters such as compounds **3** and **4** are representative of soluble low-LUMO electron acceptors for application in solution-processed OPV devices. The use of low-LUMO acceptors provides the opportunity to employ a wider range of donor materials, especially those with low LUMO levels. Further molecular design and optimization of the organic components (i.e., phenyl groups) of the fullerenyl esters sre underway to achieve high efficiencies in OPV devices.

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Supporting Information Available. Synthetic procedures, HPLC charts, NMR spectra, CV data, molecular orbitals, crystallographic data for **2a**, **3**, and **4** (CIF), and OPV performance. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

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