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Design Concept for High-LUMO-level Fullerene Electron-acceptors for Organic Solar Cells

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Abstract

This review article describes design concept, synthesis, and features of fullerene derivatives having high lowest unoccupied molecular orbital (LUMO) levels to achieve high open-circuit voltage in organic thin-film photovoltaic devices. Installation of organic electron-donating groups onto fullerene and decrease of the size of the fullerene π-electron-conjugated system raise the LUMO levels, affording high-performance organic solar cells. Addition of the methano group as the smallest carbon addend to fullerene to obtain 56π-electron fullerene derivatives is likely a promising strategy for this purpose.

♦ Introduction

Organic thin-film solar cells are lightweight and flexible, and thus are expected to allow for low-cost production through a printing process.[1] The active layer that converts light into electricity contains organic semiconductors, whose development is the key to improving power conversion efficiency. Accordingly, organic chemistry has a major role to play. Up to now, the development of organic thin-film solar cells has been led by material scientists and device engineers, but there is increasing demand for collaboration with synthetic chemists who can design and synthesize organic semiconductor molecules.

Although the power conversion efficiency of organic thin-film solar cells was about 1% before 2000, a sharp increase in conversion efficiency was seen after 2000, owing to the discovery of the combination of poly(3-hexylthiophene) (P3HT; an organic electron-donor) and phenyl-C_{61}-butyric acid methyl ester (PCBM; an organic electron-acceptor).[2] When heated and exposed to solvent vapor, P3HT undergoes self-assembly and forms π-stacked structures, improving its electrical properties and light absorption characteristics. Furthermore, PCBM is a fullerene derivative that is soluble in organic solvents, and its solubility allows for blend solutions containing P3HT to be prepared over a range of concentrations. Furthermore, thin films prepared through the use of a P3HT/PCBM blend solution have made it possible to develop composite films with a bulk heterojunction structure, in which an electron-donor and an electron-acceptor are suitably mixed.[3] In comparison with conventional p–n heterojunction devices, bulk heterojunction devices have a greater interface area between the donor and acceptor and charge separation is more efficient. In this way, around 2005, power conversion efficiency reached 4–5%.[4]

In the last few years, the power conversion efficiency of organic thin-film solar cells has increased further to about 10%.[5] This vast improvement was largely due to the development of new materials, for example, new electron-donors such as low band gap polymers,[6] which are capable of absorbing long-wavelength light. These materials are alternating copolymers with electron-rich and electron-deficient parts, and for this reason they have high-lying HOMO and low-lying LUMO levels. Intermolecular charge transfer from electron-rich parts to electron-deficient parts makes such materials capable of absorbing light with wavelengths of up to near infrared, affording higher photocurrent from the cells. On the other hand, this raises the question as to what molecular design would be suitable for the electron-acceptors. Fullerene derivatives are commonly used as electron-acceptors, and those have many advantages over fullerene itself because of their tunable supramolecular structures[7–10] and electronic structures.[11] One effective strategy might be to develop a fullerene derivative capable of giving higher voltages by changing electronic structure. In this review, we focus on fullerene derivatives that achieve high voltages, and discuss the history of their development and some useful design guidelines.

♦ Open-circuit Voltage in Organic Photovoltaic Devices

For achieving high voltage in organic photovoltaic devices, the HOMO and LUMO levels of organic semiconductors must be considered. The energy diagrams of two types of organic semiconductors (electron-donor and electron-acceptor) are shown in Figure 1. Usually, since the absorption coefficient of the electron-donor is about 10-fold that of the electron-acceptor, we focus on the case of electron-donor excited. When an electron-donor absorbs light, an electron goes from the HOMO to the LUMO, and the donor undergoes an excited state. This electron in the LUMO level of the donor transfers to the LUMO of the acceptor, affording a charge-separated state. Holes as radical cations of the donor and electrons as radical anions of the acceptor are collected at the two electrodes, generating photocurrent. A larger energy gap between the HOMO level of the donor and the LUMO level of the acceptor gives a higher open-circuit voltage. Making the HOMO level of the donor lower and the LUMO level of the acceptor higher is effective for obtaining a high open-circuit voltage. Here, we discuss fullerene acceptors with high LUMO levels.

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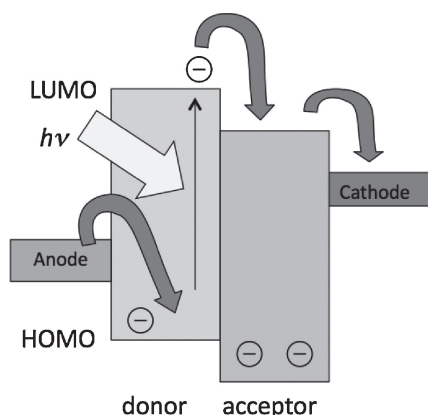*E-mail: matsuo@chem.s.u-tokyo.ac.jp*

Figure 1. Energy diagram of electron-donors and -acceptors.

♦ ### *Improvement of Open-circuit Voltage by Installation of Electron-donating Groups*

The development of fullerene derivatives with high LUMO levels was first performed with derivatization of PCBM (**1**) (Figure 2), which is the standard material used as an electron-acceptor. Hummelen et al. studied raising the LUMO level by introduction of methoxy and other electron-donating groups to the phenyl group of PCBM.[12] The higher LUMO levels due to the electron-donating groups effectively gave higher open-circuit voltages. The LUMO level of 2,3,4-$(MeO)_3$ derivative **6** was about 30 meV higher than that of PCBM, and organic thin-film solar cells containing P(MDMO–PV) (= poly[2-methoxy-5-(3,7-dimethyloctyloxy)–1,4-phenylenevinylene]) as an electron-donor exhibited a 30 mV higher open-circuit voltage. Nevertheless, this method is limited because the introduction of three methoxy groups brings about an increase in open-circuit voltage of only 30 mV.
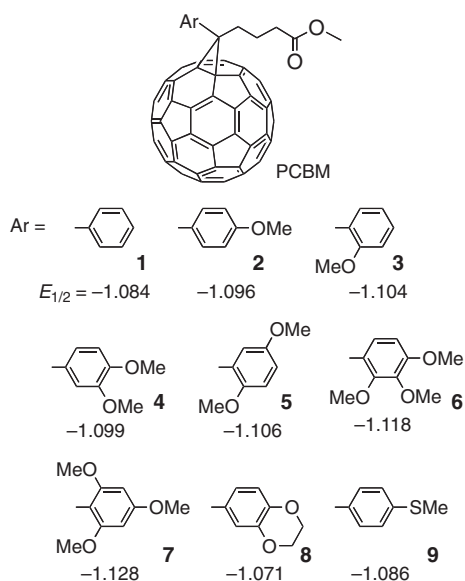

Figure 2. PCBM derivatives bearing electron-donating groups and their first reduction potentials (vs. Fc/Fc$^+$; solvent: 1,2-dichlorobenzene/acetone (1/4 v/v)).

♦ ### *Improvement of Open-circuit Voltage by Changing the Shape of Fullerene π-Systems*

In the above-mentioned method for raising the LUMO levels of fullerene by introducing electron-donating groups, the LUMO levels slightly rise, and therefore a substantial improvement in open-circuit voltage cannot be expected. A method based on changing the π-conjugated system itself has been proposed as a means for altering the LUMO level more drastically.[13] When an organic group is added to fullerene, the hybridization of the carbon atoms at the sites of addition changes from sp^2 to sp^3, and the shape of the π-conjugated system is altered. The change in shape of a fullerene π-conjugated system depends not only on the number of added organic groups, but also on the sites at which the groups are added.

In PCBM, a double bond at one site is transformed into a single bond by addition of an organic group, turning the 60π-electron-conjugated system of the original C_{60} into a 58π-electron-conjugated system. Furthermore, the carbon atoms at the sites of addition are adjacent, resulting in 1,2-addition. In this case, the contraction of the fullerene π-conjugated system is minimized. In contrast, a 1,4-addition results in a somewhat smaller 58π-electron-conjugated system due to the greater distance between addition sites. In comparison with the 58π-electron-conjugated system in the case of 1,2-addition, the system in the case of 1,4-addition exhibits a higher LUMO level and lower electron affinity.[14,15] For this reason higher open-circuit voltage is obtained from 1,4-diadducts of fullerene.[16–18]

1,4-Bis(silylmethyl)fullerene, which has a 58π-electron-conjugated system, is synthesized as follows. First, the mono-adduct $C_{60}(CH_2SiMe_2R^1)H$ is obtained by nucleophilic addition of silylmethyl Grignard reagent $R^1Me_2SiCH_2MgCl$ to C_{60} in the presence of dimethylformamide (DMF). The Grignard reagent and DMF can react with each other, and the most appropriate amount of the Grignard reagent is 10 equiv with respect to DMF. This monoaddition reaction proceeds smoothly at room temperature to reach completion within 5 min. Next, the monoadduct of fullerene anion, which is derived from deprotonation of $C_{60}(CH_2SiMe_2R^1)H$ by base, is reacted with a silylmethyl halide ($R^2Me_2SiCH_2Cl$) to produce a bisadduct $C_{60}(CH_2SiMe_2R^1)(CH_2SiMe_2R^2)$ via electrophilic substitution. If the addend is a bulky group such as a silylmethyl group, the 1,4-adduct is obtained preferentially to the 1,2-adduct. The 1,4-bis(silylmethyl)fullerene synthesized in this way is known as SIMEF, and the LUMO level of SIMEF as compared with PCBM is 60 meV higher in the case of derivative **10**,[16] where $R^1 = R^2 = Ph$, and
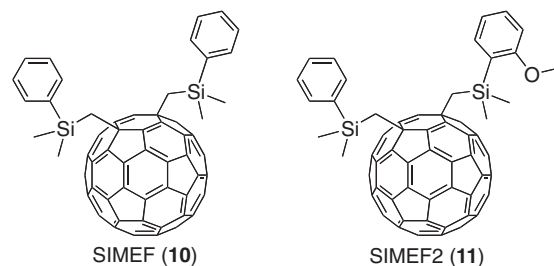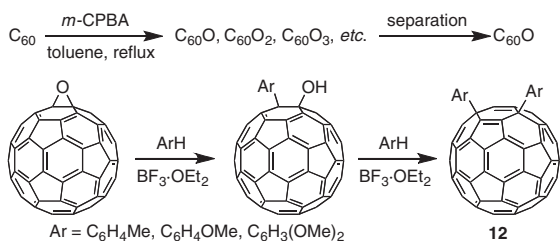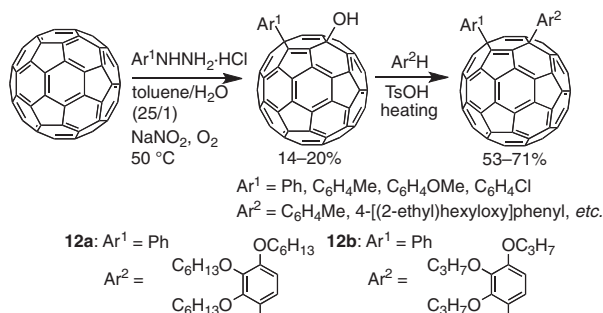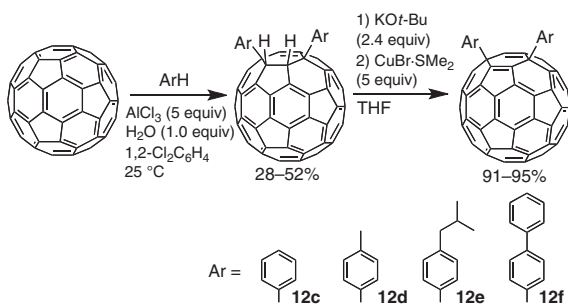

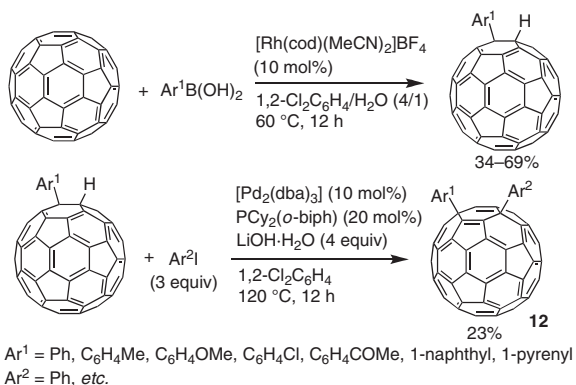**Figure 3.** 1,4-Bis(silylmethyl)fullerenes.

Scheme 1. Synthesis of 1,4-diarylfullerene via C60O.

Scheme 2. Synthesis of 1,4-diarylfullerene via fullerenol.

Scheme 3. Synthesis of 1,4-diarylfullerene by hydroarylation.

Scheme 4. Synthesis of 1,4-diarylfullerene by transition-metal-catalyzed reactions.

80 meV higher in the case of derivative **11**,[18] where R^1 = Ph and R^2 = 2-MeO-C_6H_4 (Figure 3). This brings an increase of 40–80 mV in the open-circuit voltage in photovoltaic cells.

In fullerene derivatives with direct bonding between fullerene and aryl groups, the substituent effect of the aryl group is expected to be strong. There have been several reports describing synthesis of 1,4-diarylfullerenes **12**. These reactions are the following: 1) Oxidation of C_{60} by m-chloroperoxybenzoic acid (m-CPBA) to obtain $C_{60}O$,[19] followed by the reaction with arenes in the presence of $BF_3 \cdot OEt_2$ to obtain 1,4-$C_{60}Ar_2$ through the Friedel–Crafts-type reaction via a cationic fullerene $C_{60}(OBF_3)^+$ intermediate (Scheme 1);[20] 2) reaction of C_{60} with arylhydrazine and sodium nitrite producing 1,4-$C_{60}Ar(OH)$,[21] which react with arenes in the presence of p-toluenesulfonic acid giving 1,4-$C_{60}Ar_2$ (Scheme 2);[22] 3) hydroarylation reaction of C_{60} in the presence of trichloroaluminum and a small amount of water giving $C_{60}Ar_2H_2$,[23] which is deprotonated by base, followed by oxidation of the resulting fullerene anions by copper(I) salt to produce 1,4-$C_{60}Ar_2$ (Scheme 3);[24] 4) rhodium-catalyzed addition reaction of arylboronic acids to C_{60} producing monoadducts $C_{60}ArH$,[25] which undergo palladium-catalyzed cross-coupling reaction with aryl halide to obtain 1,4-$C_{60}Ar_2$ (Scheme 4).[26]

Although diarylfullerene is a stable compound, its performance as an electron-acceptor in organic thin-film solar cells is limited. In contrast to alkyl groups, aryl groups themselves are electron-withdrawing, and therefore the LUMO levels of diarylfullerenes tend to be slightly lower than those of dialkylfullerenes. The LUMO level of many 1,4-diarylfullerenes is about the same as that of PCBM. To raise the LUMO level, phenyl groups must have electron-donating substituents. The LUMO level of compound **15a**, in which three alkoxy groups are introduced at the phenyl group, is 90 meV higher than that of PCBM. The power conversion efficiency of organic thin-film solar cells using diarylfullerenes **12b** and **12f** as electron-acceptors has been reported to be moderate (2.3%).[22,24]

♦ *Improvement of Open-circuit Voltage by Decreasing the Size of Fullerene π-Systems*

To achieve further contraction of the 58π-electron-conjugated systems of PCBM and 1,4-bisadducts, the number of additions can be increased to construct a 56π-electron-conjugated system. As organic thin-film solar cells containing such compounds achieve a very high open-circuit voltage, the use of 56π-electron fullerene derivatives is becoming increasingly widespread.

Bis-PCBM (**13**) is a 56π-fullerene derivative bearing two organic side chains (Figure 4).[27] This compound was originally
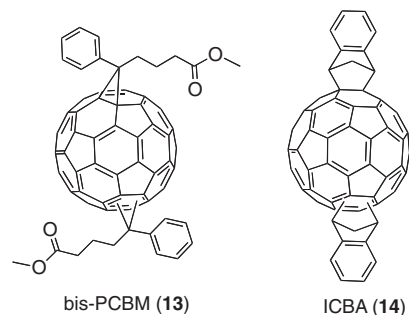

Figure 4. Examples of fullerene derivatives that have 56π-electron-conjugated systems.

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obtained as a by-product in the synthesis of PCBM, and as such it was removed. It is separated by subjecting the reaction mixture to silica gel column chromatography with a mobile phase of toluene and chloroform. Bis-PCBM is obtained as a mixture of regioisomers by removing the fractions that contain the mono-adduct PCBM and the triadduct. Although HLPC analysis performed with a Buckyprep column (mobile phase: cyclohexane/toluene = 1/1) shows three peaks, ^{1}H NMR analysis reveals 17 signals corresponding to methoxy groups, indicating a more complex mixture. Electrochemical measurements performed with the mixture itself reveal that the LUMO level of bis-PCBM is on average 100 meV higher than that of PCBM, and organic thin-film solar cells using bis-PCBM as an electron-acceptor and P3HT as an electron-donor reach a power conversion efficiency of 4.5%. In contrast to solar cells using PCBM, whose open-circuit voltage is usually 0.58 V, the open-circuit voltage of solar cells using bis-PCBM reaches 0.72 V.

Indene C$_{60}$ bisadduct (ICBA, **14**)[28–30] is obtained by addition of isoindene to C$_{60}$, where isoindene is obtained by isomerization of indene at 214 °C in 1,2,4-trichlorobenzene and other solvents with a high boiling point. Along with ICBA, this reaction also yields indene mono-, tri-, and polyadducts. By conducting silica gel column chromatography or size exclusion chromatography multiple times, the bisadduct ICBA can be isolated as a mixture of regioisomers. ICBA is highly soluble in organic solvents, with a solubility of greater than 90 mg mL^{-1}, which is due to ICBA being a mixture of regioisomers, and as such it is almost completely noncrystalline. The LUMO level of ICBA is ca. 170 meV higher than that of PCBM. Organic thin-film solar cells using ICBA achieve open-circuit voltage of ca. 0.84 V and power conversion efficiency of 5.4–6.4%.[29] The C$_{70}$ analogue IC$_{70}$BA has also been reported to improve upon the poor light absorption by ICBA in the visible region.[30]

A problem encountered in the construction of 56π-electron-conjugated systems is that steric hindrance increases together with the number of addends. Increasing steric bulkiness of organic addends other than the fullerene part hinders intermolecular contact between fullerene π-systems and thus lowers the semiconductor properties in thin films of fullerene derivatives. In particular, electron mobility is lowered, leading increase in internal resistance of the cell and lowering device performance. To achieve high power conversion efficiency, smaller organic addends are better. Because an epoxide group (an added oxygen) and an aziridine group (an added nitrogen) lower the LUMO level and raise the HOMO level, respectively, here we discuss the addition of carbon addends. The smallest carbon addend is the methylene group (CH$_2$), where we call the methylene adduct of fullerene methanofullerene.

Methanofullerene C$_{61}$H$_2$ (**15**), obtained upon the addition of a methylene group to fullerene, has been known since 1993.[31] Nevertheless, the yield of C$_{61}$H$_2$ was low at ca. 10%, and because the polarity and volume of C$_{60}$ and C$_{61}$H$_2$ are roughly the same, separation by silica gel column chromatography and size exclusion chromatography is virtually impossible; consequently, pure C$_{61}$H$_2$ has been extremely difficult to obtain. Recently, our group developed a convenient reaction for obtaining C$_{61}$H$_2$ in a high yield of 80–90% (Scheme 5).[32] Taking mono(isopropoxysilylmethyl)fullerene C$_{60}$(CH$_2$SiMe$_2$-Oi-Pr)H, which can be purified, as a key intermediate, copper(II) salt is used as an oxidizing agent. Deprotonation of the
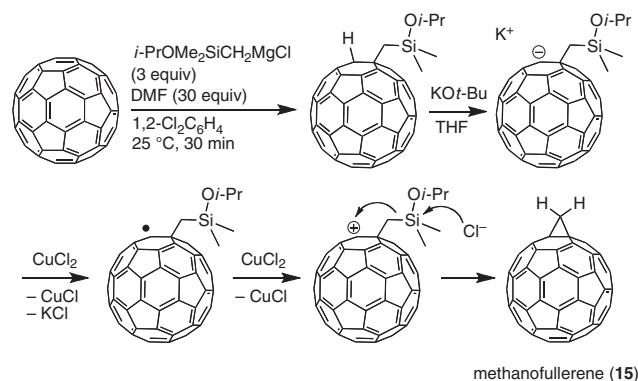
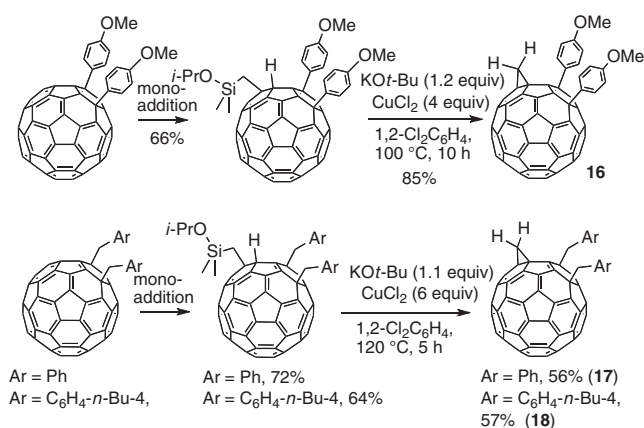**Scheme 5.** Selective synthesis of methanofullerene.
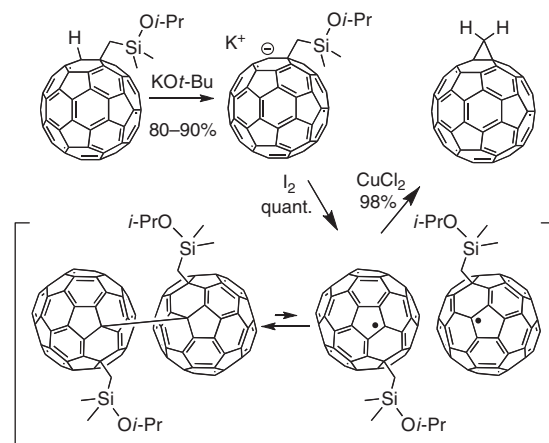
Scheme 6. Synthesis of methanofullerene via the dimer.

monoadduct with base yields fullerene monoadduct anion, which is subsequently oxidized with CuCl$_2$, producing fullerene radical and then fullerene cation. After this, the electrons of the silicon–carbon bond migrate to the fullerene cation, forming a cyclopropane ring. We consider, in this reaction, the electron-donating isopropoxy group plays an important role for this electron flow from the Si–C bond to the fullerene cation. If the electron-donation nature of the substituents on the silicon atom is insufficient, for instance the case of a phenyl group, instead 1,2-arylsilylmethyl adducts of fullerenes are obtained via migration of the phenyl group from the silicon atom to the fullerene core.[33]
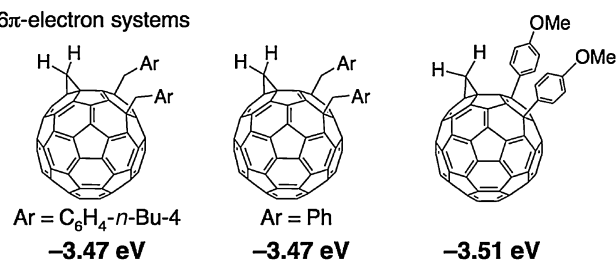
Alternatively, methanofullerene is obtained from a dimer [C$_{60}$(CH$_2$SiMe$_2$Oi-Pr)]$_2$, which is readily prepared by oxidation of the fullerene anion C$_{60}$(CH$_2$SiMe$_2$Oi-Pr)$^-$ with iodine. The dimer can be purified with silica gel column chromatography, and it is in equilibrium between the dimer and monomer radicals in solution at high temperature (ca. 100 °C). Thus, the dimer is heated in solution and reacted with CuCl$_2$ to undergo oxidation to give C$_{61}$H$_2$ via the same fullerene cation intermediate (Scheme 6). Chemical yield from the dimer is 98%.

Fullerene derivatives possessing 56π-electron-conjugated systems with the sterically small addend are obtained by introduction of the methylene group to various 1,4-bisadducts (Scheme 7). Starting from 1,4-diarylfullerene C$_{60}$Ar$_2$, the products C$_{60}$(CH$_2$)Ar$_2$ **16** are obtained by the addition of the

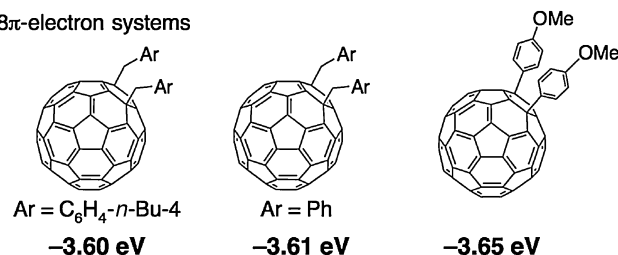**Scheme 7.** Synthesis of 56π-electron methanofullerenes.

Figure 5. Comparison of the LUMO levels between 56π- and 58π-electron fullerene derivatives.

isopropoxysilylmethyl group and subsequent cyclization through oxidation with copper(II) salt. Similarly, dialkyl methano derivatives $C_{60}(CH_2)(CH_2Ar)_2$ **17** and **18** are synthesized from 1,4-dialkylfullerene $C_{60}(CH_2Ar)_2$. Compared with the starting materials that have 58π-electron-conjugated systems, the LUMO levels of these 56π-electron derivatives are ca. 140 meV higher (Figure 5), providing high open-circuit voltage in organic photovoltaic cells. Furthermore, in contrast to bis-PCBM and ICBA, such 56π-electron-conjugated systems obtained from 1,4-adducts are not mixtures of regioisomers. Since the silylmethyl addition to the 1,4-adducts proceeds regioselectively, a single isomer of the 56π-electron product is obtained. Furthermore, structural analysis of $C_{60}(CH_2)(CH_2Ar)_2$ by X-ray crystallography confirms that the methylene group (CH_2) is indeed small and its influence on crystal packing structure is minimal. Such small groups are expected to minimize the decrease in electron mobility.

Methano-PCBM compound **19** is obtained when the side chain of PCBM is added to methanofullerene (**15**); the methano group is introduced first, and then the the side chain of PCBM is added (Scheme 8).[34] The LUMO level of this compound is
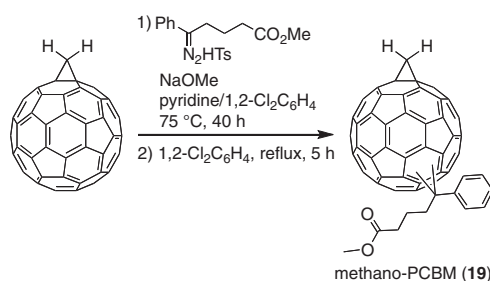
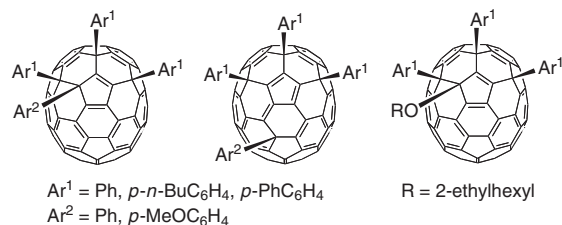**Scheme 8.** Synthesis of the methano-PCBM derivative.

Figure 6. Tetra(organo)[70]fullerenes for organic photovoltaic devices.

150 meV higher than that of PCBM, and its electron mobility is high ($0.014 \, cm^2 \, V^{-1} \, s^{-1}$) owing to the small size of the addends. Whereas PCBM in organic thin films tends to aggregate as a result of thermal annealing at high temperatures, which is known to degrade device performance, the noncrystalline compound **19**, which is a mixture of regioisomers, does not undergo such aggregation, which ensures a stable thin-film morphology and reduces the degradation over time of organic thin-film solar cells.

◆ 66π-Electron C_{70} Derivatives

Decrease in the size of π-electron-conjugated systems of C_{70} has also been done to obtain high-performance electron acceptor in organic photovoltaic devices. C_{70} derivatives show stronger light absorption than C_{60} derivatives because of larger π-conjugated systems of C_{70}, and this corresponds to higher photocurrent generated at solar cells. $IC_{70}BA^{30}$ and tetra-(organo)[70]fullerenes (Figure 6),[35] which have 66π-systems, have been developed so far. Tetra(organo)[70]fullerenes shows open-circuit voltage of 0.90 V in combination with tetrabenzo-porphyrin donor.

◆ Concluding Remarks

The improvement of the characteristics of fullerene derivatives used in organic thin-film solar cells was discussed mainly from the perspective of developing fullerene derivatives that achieve high voltage. Since fullerene itself has high electron affinity (low-lying LUMO level), it is inferior in terms of obtaining high voltage. We discussed strategies for achieving high open-circuit voltage with perspective for raising the LUMO levels, which involves introduction of electron-donating groups and contraction of the fullerene π-conjugated system. Although increasing the number of substituents in order to contract the π-conjugated system tends to lower electron mobility, using the

methano group, which is the smallest carbon addend, is expected to solve this problem. While in this paper we discussed mechanisms for raising the LUMO levels through modification of the surface of C_{60}, research is also currently being conducted by using endohedral metallofullerenes[36] and open-caged fullerenes.[37] Our hope is that this paper provides useful knowledge to researchers who perform the design and synthesis of organic semiconducting materials used in organic thin-film devices.

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