

Development of fullerene derivatives with high LUMO level through changes in π -conjugated system shape*

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Abstract: This article describes a concept for designing fullerene-based electron-accepting materials to obtain high open-circuit voltage (V_{OC}) in organic thin-film photovoltaic devices without an accompanying decrease in short-circuit current density. The keys to this concept are (1) reducing the size of the fullerene π -conjugated system to realize high V_{OC} and (2) shortening the inter-fullerene distance in the solid-state packing structure to achieve high short-circuit current density (J_{SC}), which is made possible by well-designed supramolecular organization or a small organic addend. In this article, two representative examples are discussed. One is 1,4-bis(silylmethyl)[60]fullerene (SIMEF), which forms a columnar fullerene-core array for high electron mobility and undergoes thermal crystallization for good phase separation with the electron-donating material. The other is a 56π -electron fullerene derivative bearing a dihydromethano group, the smallest carbon addend, which does not disrupt fullerene–fullerene contact in the solid state.

Keywords: cyclization; cyclopropanation; fullerenes; fullerene chemistry; organic photovoltaic devices; organic semiconductors; silicon; silylmethyl groups; solar cells; solar energy.

INTRODUCTION

Development of organic photovoltaic (OPV) devices has become an important research topic because of their promise as renewable energy technology. In organic electronic devices, fullerenes are commonly used as photoelectrochemically active materials because their high electron affinity enables efficient photoinduced electron transfer and charge separation. To achieve efficient and mechanistically well-defined photoenergy conversion, rational design of fullerene derivatives and construction of their ordered supramolecular structures in the solid state are vital. Herein we describe the design of new fullerene derivatives to achieve high-performance OPV devices, and report new fullerene-based electron acceptors, namely, 1,4-bis(silylmethyl)[60]fullerenes (SIMEFs) [1,2] and a 56π -dihydromethano[60]fullerene [3] derivative. Both allow for high open-circuit voltage (V_{OC}) without an accompanying decrease in short-circuit current density (J_{SC}).

INFLUENCE OF FULLERENE LUMO LEVEL ON V_{OC} IN OPV DEVICES

Functionalized fullerenes are obtained by chemical modification of fullerenes. The photoelectric properties of a fullerene derivative mainly depend on the size and shape of its π -conjugated system, which

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can be modified by changing the number of organic addends and their positions on the fullerene core [4]. For instance, increasing the number of addends, and thereby decreasing the size of the π -conjugated system, reduces the π -conjugation length and raises the lowest unoccupied molecular orbital (LUMO) level (Fig. 1). In an OPV device, V_{OC} is closely related to the energy gap between the highest unoccupied molecular orbital (HOMO) of the electron donor and the LUMO of the electron acceptor. Power conversion efficiency (PCE) is given by the following equation: $PCE = J_{SC} \times V_{OC} \times FF$, where FF is the fill factor. High V_{OC} is beneficial for device performance.

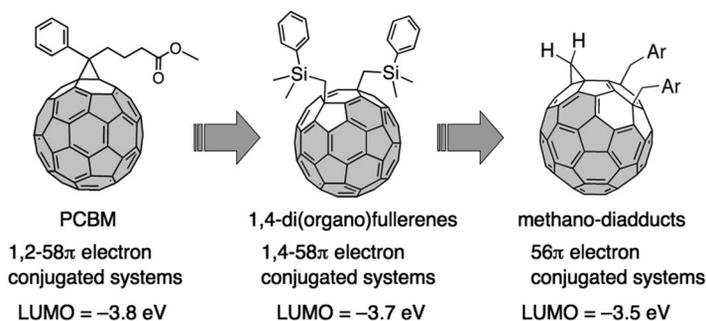
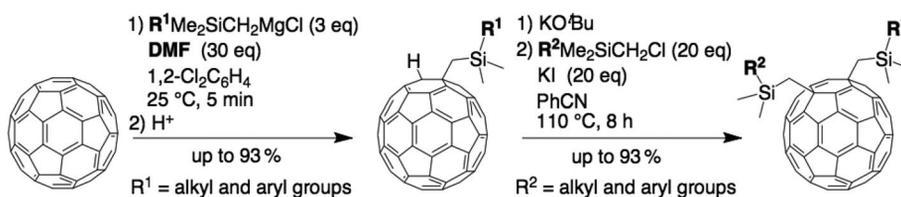


Fig. 1 Reducing the size of fullerene π -conjugated systems (shaded gray) to obtain higher LUMO levels.

1,4-DI(SILYLMETHYL)[60]FULLERENES

PCBM ([6,6]-phenyl-C61-butyric acid methyl ester) (Fig. 1) has been widely used as an organic electron acceptor in OPV devices following the report by Heeger et al. on solution-processable bulk heterojunction OPV cells in 1995 [5]. PCBM has a 58 π -electron conjugated system with a 1,2-addition pattern; the LUMO level of PCBM is -3.8 eV [LUMO level = -(4.8 eV + the first reduction potential of compound vs. Fc/Fc⁺)]. Fullerene derivatives with a 1,4-addition pattern will have smaller π -conjugated systems than those with a 1,2-addition pattern (Fig. 1), and thus we anticipated that the LUMO levels of such 1,4-diadducts will be higher owing to their lower electron affinity [1,2,6]. To investigate this hypothesis, we chose silylmethyl groups as addends for the 1,4-diadducts for the following reasons. (1) Substituents on silicon are easily changed because of the ease of Si-C bond formation compared with C-C bond formation. This allows for molecular diversity, which is important for controlling electrochemical and thermal properties, as well as for optimizing packing structure and morphology in the solid state. (2) Silylmethyl Grignard reagents are good nucleophiles and are generally used in organic synthesis. Standard electron-accepting materials in OPV research must be accessible in good yield. (3) Silylmethyl groups provide good solubility, leading to good processability for fabricating organic thin-film devices by solution-coating processes.

SIMEFs were synthesized via a two-step sequence (Scheme 1). The first step was efficient dimethylformamide (DMF)-assisted monoaddition of silylmethyl Grignard reagent to C₆₀. In this reaction, 3 equiv of Grignard reagent and 30 equiv of DMF were used to obtain the monoadducts, hydro(silylmethyl)[60]fullerene C₆₀(CH₂SiMe₂R¹)H. The reactions were run for 5–10 min at room temperature to give the products in 70–93 % yield. We surmise that DMF accelerates nucleophilic attack through coordination to magnesium in the Grignard reagent and stabilizes anionic reaction intermediates such as [MgCl(dmf)_n][C₆₀(CH₂SiMe₂R¹)] before acid treatment. The second step was simple nucleophilic substitution using a silylmethyl halide and monoadduct anion, which could be generated by deprotonation of the monoadduct with base. This reaction proceeded with complete regioselectivity to afford 1,4-diadducts C₆₀(CH₂SiMe₂R¹)(CH₂SiMe₂R²) in total yield of 50–80 % from C₆₀.



Scheme 1 Synthesis of SIMEFs via two-step sequence.

The SIMEF bearing a phenyl group on each silicon formed columnar fullerene-core arrays in its crystal packing structure (Fig. 2). This structure is induced by phase separation between spherical aromatic fullerene cores and flexible aliphatic silylmethyl side chains. The silylmethyl groups are packed in honeycomb-like pores formed by the fullerene-core arrays. Such one-dimensional alignment of the fullerene cores is expected to provide efficient electron transport pathways. In the space-charge-limited current model, SIMEF indeed exhibited higher electron mobility (8×10^{-3}) than PCBM (6×10^{-3}).

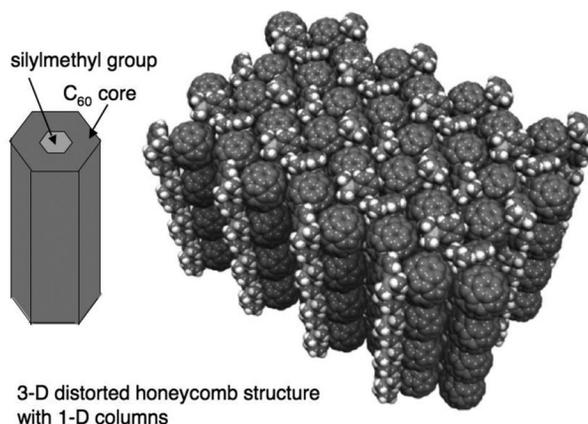


Fig. 2 Crystal packing structure of 1,4-bis[dimethyl(phenyl)silylmethyl][60]fullerene.

The thermal properties of electron-accepting materials in OPV devices strongly affect supramolecular organization and morphology in organic thin films. Thermal properties are also critical in obtaining a well-defined interface structure between electron-donating and -accepting materials. We investigated the thermal properties of 1,4-bis[dimethyl(phenyl)silylmethyl][60]fullerene by differential scanning calorimetry (DSC), and found that this SIMEF thermally crystallized at 150 °C (Fig. 3). Thus, heating an amorphous film on a substrate can afford a crystalline film. The thermal behavior can be altered by changing the substituents on each silicon. For instance, SIMEF bearing two methyl groups instead of two phenyl groups showed higher crystallinity to give a crystalline film. An asymmetric SIMEF bearing one phenyl group and one methyl group, on the other hand, amorphous, and did not crystallize upon heating.

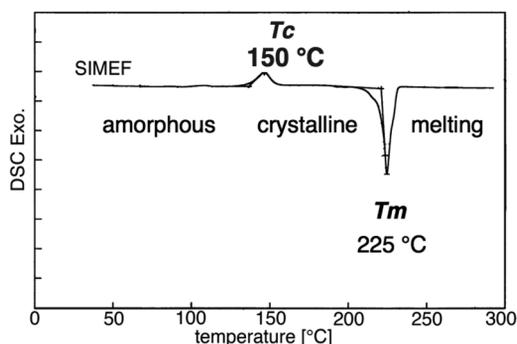


Fig. 3 Thermal properties of 1,4-bis[dimethyl(phenyl)silylmethyl][60]fullerene.

We fabricated three-layered p-i-n type OPV cells using SIMEF as the electron acceptor and a tetrabenzoporphyrin (BP, Fig. 4) precursor (CP), which was thermally converted into BP at 150–180 °C. BP then served as the donor material. Subsequent wet-coating and thermal conversion processes for the p (BP), i (BP and SIMEF), and n (SIMEF) layers afforded p-i-n devices in which the i layer had a well-defined interdigitated structure on a nanometer scale. This suitable structure formed through thermal co-crystallization of BP and SIMEF in the organic thin film. Heating the blended mixture of CP and SIMEF starts both the thermal conversion of CP to BP and crystallization of SIMEF at the same temperature, giving fine, columnar crystals of BP through restricted nanoscale phase separation between BP and SIMEF. BP crystals with diameter of 25 nm and height of 65 nm (Fig. 4) enabled efficient exciton dissociation and charge transport. The device showed PCE of 5.2 % with good V_{OC} (0.75 V) and J_{SC} (10.5 mA/cm²) under air-mass 1.5 global (AM 1.5) illumination with intensity of 100 mW/cm². The higher V_{OC} of this device than that of PCBM-based devices corresponds to the higher LUMO level of SIMEF. When OPV devices have good V_{OC} , there is typically a trade-off where J_{SC} becomes lower. This device, however, showed high J_{SC} and good FF (0.66). This result is likely related to the good packing structure of SIMEF.

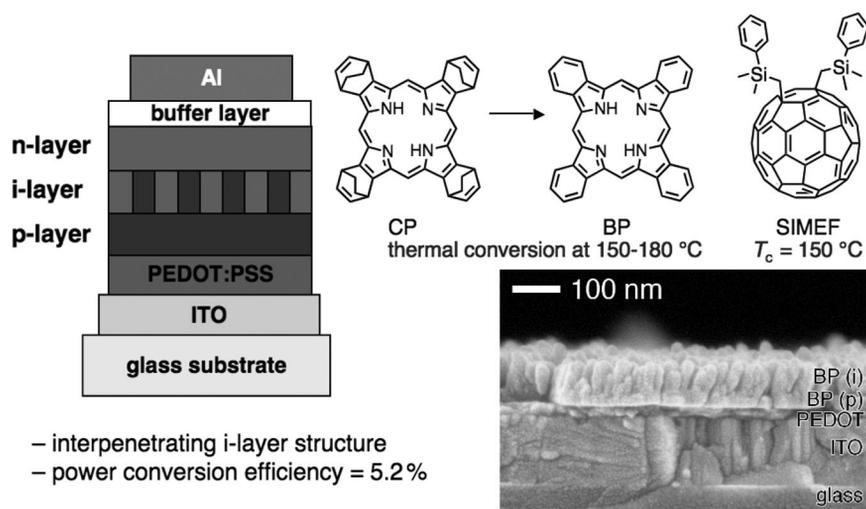
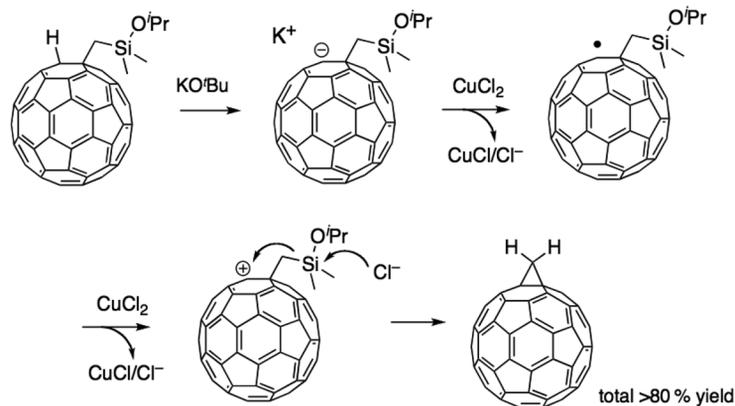


Fig. 4 Three-layer p-i-n OPV device using SIMEF and BP. SEM image shows BP nanocrystals in the i layer.

DIHYDROMETHANO[60]FULLERENES WITH 56 π -ELECTRON CONJUGATED SYSTEM

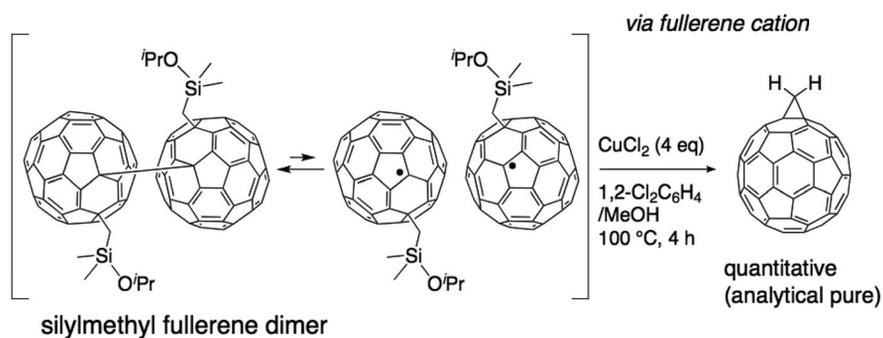
Next, we will discuss the strategy of substantially decreasing the size of the fullerene π -conjugated system. Recently, 56 π -electron fullerenes such as bis-PCBM [7] and indene C_{60} bis-adduct (ICBA) [8–12] have received much attention, because they have high LUMO levels and thus give high V_{OC} values in photovoltaic applications. However, such 56 π -electron fullerenes have the drawback of low electron mobility, owing to their many bulky organic addends, which tend to disrupt close fullerene–fullerene contact. Our idea is based on the use of the smallest possible carbon addend, the methylene group (CH_2), to realize close fullerene–fullerene contact and thus enable good electron transport, giving high J_{SC} and FF in OPV applications.

Several synthetic methods for 1,2-dihydromethano[60]fullerene $C_{61}H_2$ have been reported since 1993 [13]. In addition to very low yield, there are insurmountable problems in the separation and purification processes when such methods are employed. Since the starting material C_{60} and the product $C_{61}H_2$ have similar polarity and size, silica gel column chromatography and size exclusion chromatography are ineffective. It is thus necessary to develop a new way for efficiently synthesizing $C_{61}H_2$. We found that oxidation of silylmethyl[60]fullerene anion with Cu(II) chloride affords a cyclopropanated product $C_{61}H_2$ via a cationic fullerene intermediate (Scheme 2) [3]. Treatment of isopropoxysilylmethyl[60]fullerene anion $C_{60}(CH_2SiMe_2O^iPr)^-$ with oxidant $CuCl_2$ afforded cationic intermediate $C_{60}(CH_2SiMe_2O^iPr)^+$, which undergoes a concerted reaction involving electron flow from the Si–C(methylene) bond to the fullerene cation to form the C(fullerene)–C(methylene) bond and nucleophilic attack of the chloride anion at silicon. The electron-donating nature of the isopropoxy group enhances the electron flow. Total yield for deprotonation of the monoadduct $C_{60}(CH_2SiMe_2O^iPr)H$ and oxidation was 80 %. Note that the deprotonation step is not quantitative, resulting in lower total yield.



Scheme 2 Synthesis of 1,2-dihydromethano[60]fullerene through Cu(II)-mediated oxidation of silylmethyl[60]fullerene anion.

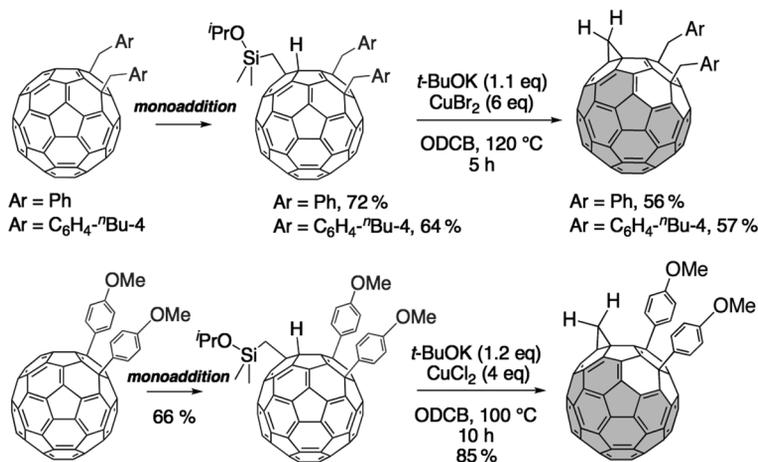
Alternatively, starting from a dimer $[C_{60}(CH_2SiMe_2O^iPr)]_2$, which was readily prepared by oxidation of the fullerene anion $C_{60}(CH_2SiMe_2O^iPr)^-$ with iodine, a similar reaction gave the methanofullerene product in quantitative yield (Scheme 3). Singly bonded fullerene dimers are known to thermally generate monomer radical [14], which can undergo oxidation and cyclization under the above-mentioned reaction conditions. The dimer can be purified by silica gel column chromatography. Thus, this reaction can be performed using the purified dimer to obtain an analytically pure product without the need for further chromatographic purification. An added benefit is that this reaction can be conducted in air. Although it is reasonable to expect reaction between the intermediate fullerene radi-



Scheme 3 Synthesis of 1,2-dihydromethano[60]fullerene starting from dimer.

cal and molecular oxygen, such aerobic oxidation was not observed. We surmise that thermally generated radical species were immediately oxidized by Cu(II) for clean conversion to the cyclized product.

Having found a suitably workable reaction, we synthesized 56π -electron fullerene derivatives starting from 58π -electron 1,4-diadducts. Monoaddition of the isopropoxysilylmethyl group onto 1,4-di(organo)[60]fullerenes produced tri(organo)[60]fullerenes $C_{60}R_2(CH_2SiMe_2O^iPr)H$ and $C_{60}Ar_2(CH_2SiMe_2O^iPr)H$ in moderate yield (Scheme 4). Deprotonation and oxidation were carried out to construct the methano group, giving 56π -electron fullerenes possessing the smallest possible organic addend. These products have suitable LUMO levels in a range from -3.4 to -3.5 eV (Fig. 5). Reducing the size of the π -conjugated system of 1,4-di(organo)[60]fullerenes led to a 0.15 eV increase in their LUMO levels.



Scheme 4 Synthesis of 56π -electron fullerenes bearing methano group.

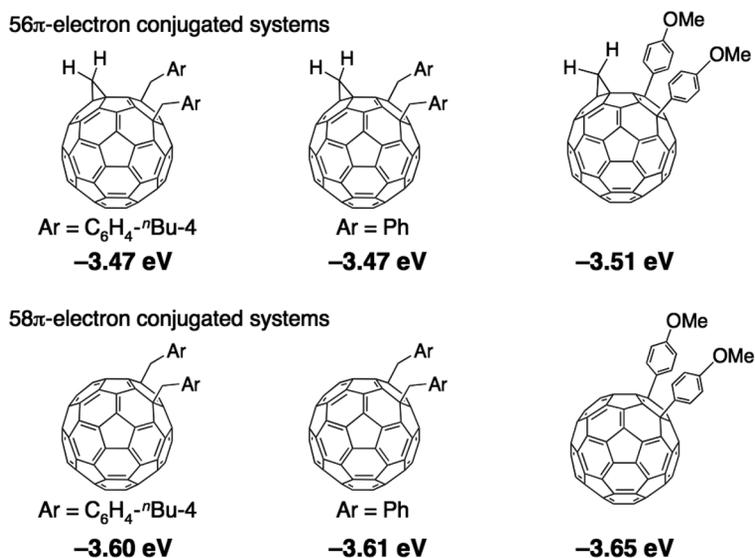


Fig. 5 Comparison of LUMO levels of 56 π -electron fullerenes and their parent 58 π -electron 1,4-di(organo)[60]fullerenes.

We fabricated standard P3HT-based bulk heterojunction OPV devices using a 56 π -electron dihydromethano[60]fullerene (C₆₀(CH₂)(CH₂C₆H₄-*n*Bu-4)₂) as the electron-accepting material. The device showed higher V_{OC} (0.82 V) than the reference device using PCBM (0.58 V). J_{SC} (7.1 mA/cm²) was not notably lower than that of the reference device (7.4 mA/cm²). Here, a 41 % higher V_{OC} was accompanied by only a 4 % lower J_{SC} ; this result compares favorably with previous reports where such an improvement in V_{OC} typically came with decreasing J_{SC} .

CONCLUSION

We have presented a concept for designing fullerene-based electron-accepting materials in OPV devices to obtain high V_{OC} without an accompanying decrease in J_{SC} . SIMEFs have a 1,4-addition pattern which allows for higher V_{OC} compared with fullerene derivatives having a 1,2-addition pattern. There is considerable synthetic flexibility for the silicon substituents, which allows for molecular diversity and thermal formation of one-dimensional fullerene arrays. Such arrays are good for electron transport to realize high J_{SC} and FF. The smallest possible carbon addend, the methano group, was efficiently installed on 58 π -electron fullerenes to give 56 π -electron dihydromethano[60]fullerenes that have higher LUMO levels than the parent fullerenes. Consequently, OPV devices that had higher open-circuit voltage could be fabricated. The small methano group permits close fullerene–fullerene contact, thus minimizing the J_{SC} drop in the OPV devices. We expect that this new design concept will work well in the development of high-performance OPV devices.

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