ARTICLE TYPE

Modification of σ-framework of [60]fullerene for bulk-heterojunction solar cells

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Modification of the σ-framework of [60]fullerene have been shown to be a new avenue toward n-type materials for bulk-heterojunction solar cells. This approach allowed distinct
10 **control of the LUMO level of the C_{60} π-system and resulted in a clear improvement of an open-circuit voltage.**

π-Conjugated semiconductor materials have occupied a dominant position in organic thin-film photovoltaic devices, so called bulk-heterojunction (BHJ) solar cells.[1] The core of the device is a
15 single active layer which typically consists of a blend of electron-donating polymer, such as poly(3-hexylthiophene) (P3HT), and electron-accepting molecule, such as (6,6)-phenyl C_{61}-butyric acid methyl ester (PCBM).[2] In the light of easy fabrication through solution process, flexibility, and large area application,
20 the BHJ solar cell will be a potential alternative to conventional silicon-based solar cell, if the low power conversion efficiency (PCE) is overcome.[1] During the last few years the PCEs have been rapidly improved largely owing to development of a wide variety of donor copolymers made of electron-rich and electron-
25 poor building blocks with enhanced absorptions in the visible area.[3]

It is well known that electronic properties of the donor polymers should be controlled to match those of the acceptors. For instance, the energy level of the lowest unoccupied molecular
30 orbital (LUMO) of the donor is required to be higher than that of the acceptor by 0.3–0.5 eV to overwhelm the binding energy of excitons.[1] Under the circumstances of the rapidly extended repertoire of the low band gap polymers,[1,3] establishment of new methodology capable of tuning the electronic properties of the
35 [60]fullerene is of increasing significance for creating rational acceptor/donor pair. However, most studies on the acceptors have so far been focused on the structural modification of the benchmark acceptor, PCBM, toward raising its LUMO energy level by (i) installation of electron-donating group(s) on its
40 phenyl ring,[4] (ii) saturation of one more C=C double bond on the fullerene cage to give almost inseparable mixture of regioisomers,[5] and (iii) encapsulation of a trimetallic nitride cluster inside C_{80} cage to give the endohedral $PC_{81}BM$ analogs.[6] As another approaches, 1,4-di(organo)C_{60} derivatives[7a] and
45 indene-C_{60} bisadduct[7b] were recently reported.

During our studies on organic synthesis of endohedral fullerenes encapsulating small gaseous entities,[8,9] so called

molecular surgery,[10] we have established techniques to modify the σ-framework of fullerenes to create a wide opening. The
50 unique features of the skeletally-modified fullerenes (SMFs) lie in the retention of the 60π- or 70π-conjugated systems as well as appearance of rich chemical reactivity at the opening.[11] Actually, as we reported recently, the opening of SMF derivative **1** could be effectively transformed to that of **2** and **3**.[12] These SMF
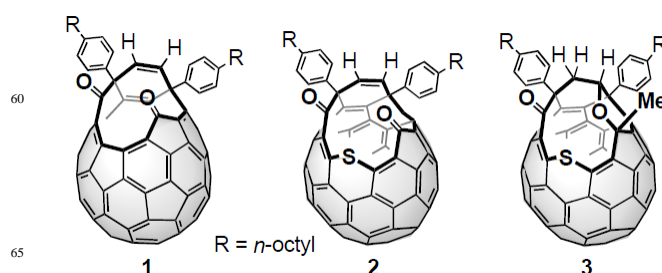55 derivatives have excellent solution processability due to two *n*-octyl chains.

Table 1 Electrochemical reduction potentials[a] of C_{60}, SMFs **1–3**, and PCBM, and calculated LUMO levels[b]

Compound	E_{red}^1 (V)	E_{red}^2 (V)	E_{red}^3 (V)	LUMO (eV)
C_{60}	−1.09	−1.49	−1.95	−3.23
1	−1.00	−1.40	−2.03	−3.32
2	−1.12[c]	−1.52[c]	−2.01[c]	−3.18[c]
3	−1.23[c]	−1.62[c]	−2.14[c]	−3.00[c]
PCBM	−1.17	−1.57	−2.09	−3.04

[a] Values for $0.5(E_{pa} + E_{pc})$ in V vs. Fc/Fc$^+$; in $1,2\text{-}Cl_2C_6H_4$ with 0.1 M Bu_4NBF_4 as supporting electrolyte; Pt wire as counter electrode and glassy carbon as working electrode; scan rate of 20 mV s^{-1}. [b] Calculated at the B3LYP/6-31G* level of theory with replacement of the *n*-octyl groups to methyl groups. [c] Values taken from ref. 12.

70 Electrochemical reduction potentials of SMFs **1–3**, C_{60}, and PCBM investigated by cyclic voltammetry (CV) are summarized in Table 1 together with calculated LUMO energy levels.[13] All SMFs **1–3** exhibited pseudo-reversible first to third reduction waves in the same manner as those for C_{60} and PCBM. It is worth
75 noting that the first reduction potentials (E_{red}^1) of SMFs **2** and **3** markedly shifted to negative upon the simple modifications from **1**, that is, the sulfur insertion caused the negative shift by $\Delta E_{red}^1 = 120$ mV and the functionalization of the carbonyl group resulted in the further negative shift by $\Delta E_{red}^1 = 110$ mV, as supported by
80 the results of DFT calculations. Thus, the present approach

provides useful way to control the LUMO energy level of C_{60} without causing significant loss of the native π-conjugation. Since an open-circuit voltage (V_{oc}) has an association with the energy difference between acceptor's LUMO and donor's HOMO,[14] the higher LUMO energy level of **3** than that of PCBM should contribute to improve the V_{oc} of the device when **3** is combined with a donor polymer with an adequately high LUMO level. On the other hand, UV-vis absorption spectra showed slightly enhanced absorption bands in a range of 300–500 nm for **1**–**3** with reference to PCBM (Fig. 1).
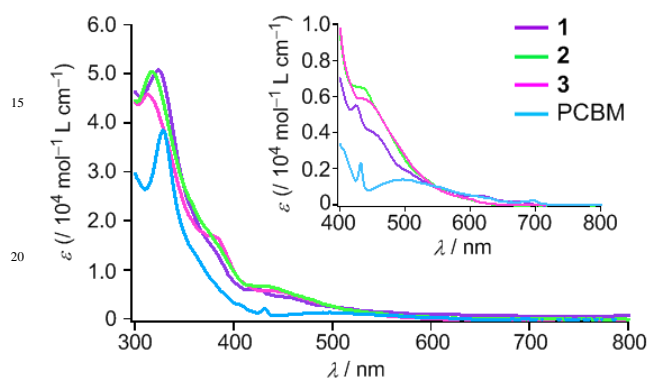

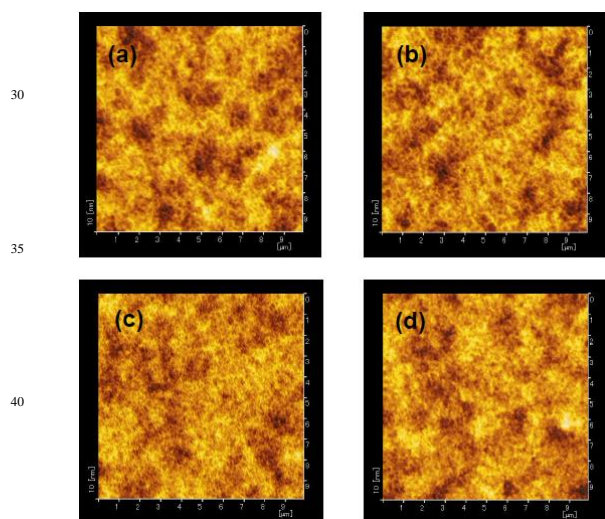**Fig. 1** UV-vis absorption spectra of **1**–**3** and PCBM in cyclohexane.

Fig. 2 Tapping mode AFM images (10 μm × 10 μm) of blend films composed of (a) **1**:P3HT, (b) **2**:P3HT, (c) **3**:P3HT, and (d) PCBM:P3HT measured after annealing.

In order to observe the effects of controlled LUMO levels of SMFs on the open-circuit voltage, BHJ solar cells were fabricated using **1**–**3** as the acceptor with a combination of the representative donor polymer, P3HT, by basically following the procedure established for PCBM:P3HT-based device.[15] The devices with a layered structure of glass/ITO/PEDOT:PSS/SMF:P3HT/TiO$_x$/Al were prepared as follows. The chlorobenzene solutions containing an SMF derivative and P3HT at weight ratio of 1 : 1.6 were spin-coated onto an indium tin oxide (ITO)/glass substrate covered with

PEDOT:PSS layer under argon, and the resulting films were annealed at 150 °C for 6 min to induce phase separation. Then, TiO$_x$ layer was coated on the active layers in air and subsequently aluminum electrode was thermally deposited under vacuum. The optimum thickness of the BHJ films was approximately 80 nm. The surface morphology of the active layers of **1**:P3HT, **2**:P3HT, **3**:P3HT, and PCBM:P3HT as a standard reference were observed by the use of atomic force microscopy (AFM) (Fig 2). All films using **1**–**3** showed fine features similar to that using PCBM. The root mean square (rms) roughness was 1.0 nm for **1**:P3HT, 0.9 nm for **2**:P3HT, 1.1 nm for **3**:P3HT, and 1.0 nm for PCBM:P3HT, respectively, indicating that the domain size of all blend films was almost identical regardless of the skeleton-modifications of C_{60} and the introduction of the *n*-octyl chains.
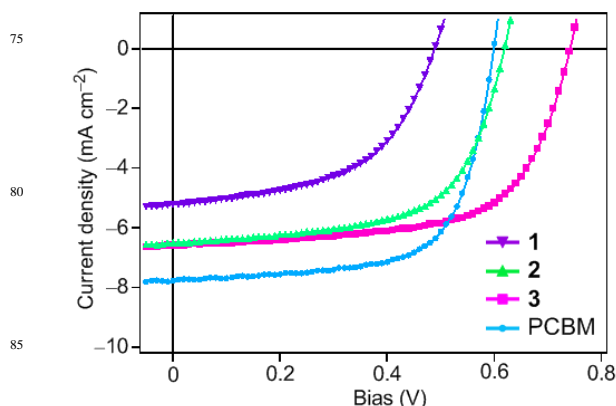

Fig. 3 Current density–voltage (*J*–*V*) characteristics of BHJ solar cells based on the active layers of **1**–**3**:P3HT and PCBM:P3HT under AM 1.5G illumination from a calibrated solar simulator.

Table 2 Characteristics of bulk-heterojunction solar cells[a]

active layer	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	η_e (%)
1:P3HT	0.49	5.20	0.53	1.35
2:P3HT	0.62	6.49	0.62	2.49
3:P3HT	0.74	6.57	0.64	3.11
PCBM:P3HT	0.60	7.76	0.67	3.12

[a] Open-circuit voltage (V_{oc}), short-circuit current density (J_{sc}), fill factor (FF), and PCE (η_e) with **1**–**3** and PCBM as the acceptor materials and P3HT as the donor material. The active area of the device is 5.2 mm^2.

The typical current density–voltage curves for the BHJ solar cells under AM 1.5G conditions of 100 mW cm^{-2} are shown in Fig. 3 and the device performances are summarized in Table 2. Actually, as expected, **1**:P3HT-based device marked a low V_{oc} value (0.49 V), reflecting the relatively low-lying LUMO energy level. This value was clearly improved to V_{oc} = 0.62 V for **2**:P3HT-based device and further to V_{oc} = 0.74 V for **3**:P3HT-based device. As shown in Fig. 4, the linear regression indicated the clear correlation (r^2 = 1.0) between the LUMO energy levels of the SMF derivatives and the V_{oc} values, although the point for PCBM:P3HT appears to deviate downward. It is worth noting that the V_{oc} of **3**:P3HT-based device was superior to that of PCBM:P3HT device (V_{oc} = 0.60 V) by ΔV_{oc} = 140 mV. This ΔV_{oc} is much larger than the value achieved by the introduction of electron-donating groups on the phenyl ring of PCBM (ΔV_{oc} =

~30 mV).[4a] These data demonstrated that the SMF derivatives are potential n-type materials with tunable LUMO levels for BHJ solar cells.
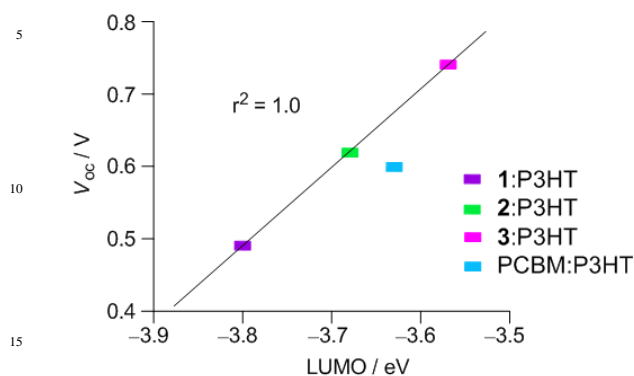

Fig. 4 The open-circuit voltages (V_{oc}) of BHJ solar cells using **1–3** and PCBM as the acceptor materials and P3HT as the donor material, plotted against LUMO levels of the acceptor materials estimated based on the first reduction potentials (E_{red}^1, V vs. Fc/Fc$^+$) on CV with the equation; LUMO level = $-(E_{red}^1 + 4.8)$.[16] Linear regression was carried out with the data for **1–3**:P3HT.

On the other hand, the short-circuit current densities (J_{sc}) of **2**:P3HT and **3**:P3HT-based devices (J_{sc} = 6.49 and 6.57 mA cm^{-2}, respectively) slightly decreased with reference to that of PCBM:P3HT-based device (J_{sc} = 7.76 mA cm^{-2}), while the fill-factors (FF) were almost identical. One possible reason would be that the presence of two *n*-octyl chains prevented the effective intermolecular π-π interaction between C_{60} cages and hence decreased the charge mobility.[17] As a result, in the combination with P3HT, the device using **3** provided the best PCE (η_e = 3.11%), which is comparable to that of the benchmark PCBM:P3HT-based device (η_e = 3.12%).[18] The particularly low values of J_{sc} (5.20 mA cm^{-2}) and FF (0.53) obtained for **1**:P3HT-based device probably resulted from the increased charge recombination in BHJ film. Actually, the shape of the LUMO was relatively localized at the opening (see the Supporting Information). The almost completely delocalized LUMOs of **2** and **3** as well as PCBM are considered to contribute to their improved J_{sc} and FF.

In summary, we have demonstrated that the structural manipulation of the C_{60} skeleton is a promising approach for the creation of acceptor materials for BHJ solar cells. This approach can be used to effectively control the electronic properties of the C_{60} moiety with the original 60π-conjugation being largely retained to rationally match the LUMO level to that of the donor materials. Actually, by combining the SMF derivatives with typical donor polymer, P3HT, we obtained the higher V_{oc} value of 0.74 V than that of PCBM:P3HT-based device by ΔV_{oc} = 140 mV. In order to improve the performance of the BHJ solar cells, it is also indispensable to enhance the carrier mobility. We are currently studying the structural optimization of the substituents toward improvement of the morphology in the BHJ films.

Notes and references

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† Electronic Supplementary Information (ESI) available: Procedure for the fabrication of the BHJ solar cells and detailed results of the electrochemical measurements, the UV-vis absorption spectra, and DFT calculations. See DOI: 10.1039/b000000x/

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