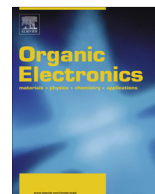




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Electronic structure of fullerene derivatives in organic photovoltaics

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ABSTRACT

The electronic structures of the fullerene derivatives [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM), [6,6]-diphenyl C₆₂ bis (butyric acid methyl ester) (bisPCBM), C₇₀, [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM), [6,6]-phenyl-C₆₁-butyric acid butyl ester (PCBB), [6,6]-phenyl-C₆₁-butyric acid octyl ester (PCBO), [6,6]-thienyl-C₆₁-butyric acid methyl ester (TCBM), and indene-C₆₀ bisadduct (ICBA), which are frequently used as *n*-type materials in organic photovoltaics, were studied by ultraviolet photoelectron spectroscopy and inverse photoemission spectroscopy. We also performed molecular orbital calculation based on density functional theory to understand the experimental results. The electronic structures near the energy gap of the compounds were found to be governed predominately by the fullerene backbone. The side chains also affected the electronic structures of the compounds. The ionization energy and electron affinity were strongly affected by the number of carbons and functional groups in the side chain.

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1. Introduction

Organic photovoltaics (OPV), particularly OPV devices containing a polymer/fullerene-based bulk heterojunction (BHJ), have attracted much interest because of their potential for low-cost, large-area, lightweight, and flexible devices with simple structures [1–3].

The fullerenes C₆₀ and C₇₀ and their derivatives bearing various functional group side chains have been used as *n*-type semiconductor materials in OPV devices with high-efficiency photoelectric conversion [4–8]. C₆₀ and C₇₀ are incompatible with solution processes because of their low solubility in common organic solvents. Soluble derivatives have been synthesized by adding functional groups to these fullerene backbones [9,10], thus allowing OPV devices to be fabricated using solution processes such

as spin-coating [11]. [6,6]-Phenyl-C₆₁-butyric acid methyl ester (PCBM) is a well-known soluble derivative and has been frequently used as an acceptor in OPVs [4,9]. Electronic structure of the fullerene derivatives has been investigated by some groups so far [12–16]. It has been reported that the side chains of PCBM and [6,6]-phenyl-C₇₁-butyric acid methyl ester (PC₇₀BM) affect the solubility and morphology of the film, and its electronic structure, which may improve device performance [14–16].

OPV performance, particularly optical absorption, carrier injection, and carrier transport, strongly depends on the electronic structure of the donor and acceptor molecules [17,18]. The electronic structure around the Fermi level (*E_F*), such as the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), plays an important role in determining the optical and transport properties [19]. For example, the correlation between the electronic structure of the donor or acceptor molecules and the open-circuit voltage (*V_{OC}*) of the device, which is an energetic driving force for electron transfer

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80 from the donor to the acceptor, is still not fully understood.
81 It is thought that V_{OC} is related to the difference between
82 the LUMO energy of the acceptor and the HOMO energy
83 of the donor [20,21]. Furthermore, the excitons, which
84 are created after light absorption and migrate to the
85 donor/acceptor interface, separate into electrons in the
86 LUMO of the acceptor and holes in the HOMO of the donor.
87 Thus, understanding the electronic structures of donor and
88 acceptor molecules is important for elucidating the mechan-
89 isms by which OPV devices operate and for optimizing
90 materials for high-performance devices.

91 Akaike et al. [14,15] reported the effects of the side chain
92 on the electronic structure of PCBM and [6,6]-diphenyl C_{62}
93 bis(butyric acid methyl ester) (bisPCBM). They concluded
94 that a subtle charge transfer from the side chain to the C_{60}
95 backbone destabilizes the electronic states of the molecule.
96 They also suggested that the effects of the side chain on the
97 electronic structures of PCBM and bisPCBM may improve
98 the performance of the OPV devices compared with devices
99 containing C_{60} [22,23]. Their work demonstrates that
100 measures of OPV device performance, such as V_{OC} , J_{SC} , and
101 fill-factor, can be discussed in terms of electronic structure.
102 There are few other studies of the electronic structure of
103 fullerene derivatives.

104 The purpose of this study is to systematically investi-
105 gate the electronic structure of the fullerene derivatives
106 used in OPVs. Fundamental information about the
107 electronic structure of fullerene derivatives can be
108 expected to guide the synthesis of new molecules
109 optimized for high-performance OPVs. The electronic
110 structures of the fullerene derivatives PCBM, bisPCBM,
111 C_{70} , $PC_{70}BM$, [6,6]-phenyl- C_{61} -butyric acid butyl ester
112 (PCBB), [6,6]-phenyl- C_{61} -butyric acid octyl ester (PCBO),

[6,6]-thienyl- C_{61} -butyric acid methyl ester (TCBM), 113
indene- C_{60} monoadduct (ICMA), and indene- C_{60} bisadduct 114
(ICBA) (Fig. 1) were examined by ultraviolet photoelectron 115
spectroscopy (UPS) and inverse photoemission spectroscopy 116
(IPES). To interpret the experimental results, molecu- 117
lar orbital (MO) calculations were performed. 118

The electronic structures of the fullerene derivatives 119
strongly depended on structural features, including the 120
type of backbone, number of side chains, side chain length, 121
and functional groups. We investigated the effect of side 122
chains by comparing C_{70} with $PC_{70}BM$ using the same 123
method as Akaike et al. [14,15] The dependence of the elec- 124
tronic structure on the fullerene backbone and the side 125
chain length are discussed by comparing PCBM, $PC_{70}BM$, 126
PCBB, and PCBO. The difference in electronic structure 127
caused by replacing a phenyl group with a thienyl group 128
in the side chain is also investigated by comparing PCBM 129
with TCBM. The effect of introducing a different type of 130
side chain on the electronic structure was examined by 131
investigating ICBA. 132

2. Experimental and theoretical procedures 133

PCBM (>99.9%), bisPCBM (mixture of isomers, 99.5%), 134
 C_{70} (99%), $PC_{70}BM$ (mixture of isomers, 99%), PCBB 135
(>97%), PCBO (>99%), TCBM (>99%), and ICBA (99%) were 136
purchased from Sigma-Aldrich and used as received. 137

Thin films of PCBM, bisPCBM, $PC_{70}BM$, PCBB, PCBO, 138
TCBM, and ICBA were spin-coated from chlorobenzene 139
solution (0.4 wt%) in a glovebox filled with N_2 at room 140
temperature. The films were spin-coated onto indium tin 141
oxide (ITO)-coated glass substrates at 1500 rpm for 30 s 142
and transferred to a vacuum chamber under N_2 . The 143

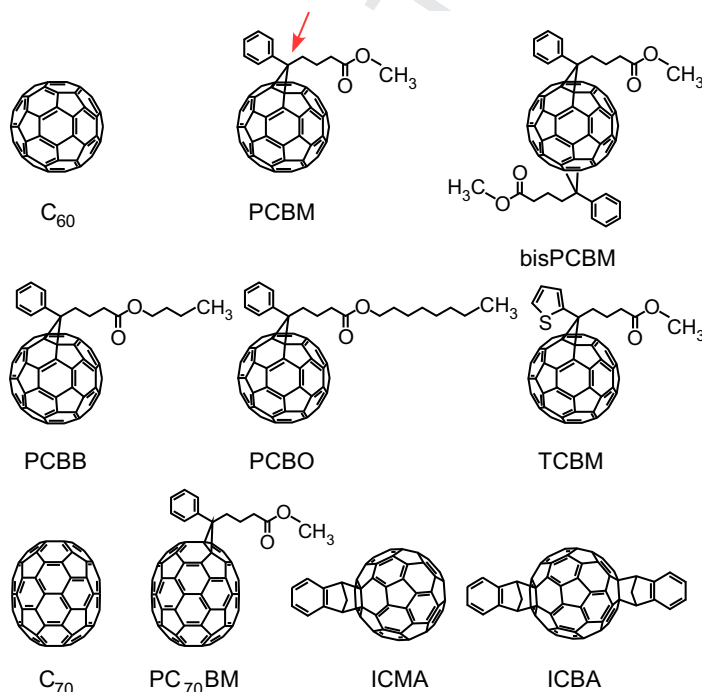


Fig. 1. Molecular structures of fullerenes and derivatives: C_{60} , PCBM, bisPCBM, PCBB, PCBO, TCBM, C_{70} , $PC_{70}BM$, ICMA, and ICBA.

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