Ambipolar Characteristics of Dendritic Oligothiophene/Fullerene Linkage Molecules

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The dendritic oligothiophene/[60]fullerene linkage molecules have been synthesized, and their electronic properties were characterized by spectroscopic and electrochemical measurements. The FET devices were fabricated with their spin-coated films and their performances were investigated.

For the design of efficient organic integrated circuits, there is an urgent need for advanced organic materials. Ambipolar organic field-effect transistors (OFETs), which work as both p- and n-channel transistors, have been demonstrated by using heterostructure[1] and heterogeneous blends[2,3] of p- and n-type organic semiconductors. As the rather simple device structures, ambipolar transistors composed by a single organic material have also been demonstrated.[2,4] However, there are not many examples of ambipolar OFETs especially using solution-fabricated organic films,[5] which have advantages for application to easy processing, flexible, and large-area devices. These ambipolar materials possess also a large potential for application to photovoltaic devices (plastic solar cells).[6] Recently, we have reported an ambipolar OFET using the oligothiophene 16-mer attached with two [60]fullerenes (**16T-2C$_{60}$**).[7] We have also developed the highly branched dendritic oligothiophenes[8] that revealed self-association behavior in solution owing to strong π–π stacking interactions and field-effect hole mobility comparable to those of long oligothiophenes.[9] Therefore, the combination of dendritic oligothiophenes and [60]fullerene is expected to form effective both hole- and electron-transporting channels in a film. In this communication, we report the synthesis, spectroscopic and electrochemical properties, and ambipolar characteristics of dendritic oligothiophenes/[60]fullerene linkage molecules (Chart 1).

We employed a convergent method with repeating Stille coupling reactions for the preparation of dendritic-oligothiophene aldehyde derivatives **Gn-CHO** ($n = 1$–3) composed by dihexylquaterthiophenes (4T) and 1,3,5-trisubstituted-benzene juncture units. The synthetic route and details are described in the Supporting Information.[10] The aldehydes **Gn-CHO** were converted to the mono-substituted [60]fullerene compounds **Gn-C$_{60}$** ($n = 1$–3) in 36–59% yields by the treatment with C$_{60}$ and *N*-methylglycine (Prato's method)[11] in refluxing chlorobenzene. Further addition reactions of **Gn-CHO** to **Gn-C$_{60}$** under the Prato's conditions gave two-dendron-substituted [60]fullerenes (**Gn)$_2$-C$_{60}$** ($n = 1$–3, 40–94%) as a mixture of several regioisomers, which was not separated and used for the following spectroscopic measurements as such.

The UV–vis absorption and photoluminescence spectra of **Gn-C$_{60}$** and (**Gn)$_2$-C$_{60}$** in *o*-dichlorobenzene were shown in Figures 1 and S1,[10] respectively, and their data were summarized in Table S1.[10] The strong absorption bands appeared in the

Gn-C$_{60}$
Ar = G1: **G1-C$_{60}$**
   = G2: **G2-C$_{60}$**
   = G3: **G3-C$_{60}$**

(Gn)$_2$-C$_{60}$
Ar = G1: **(G1)$_2$-C$_{60}$**
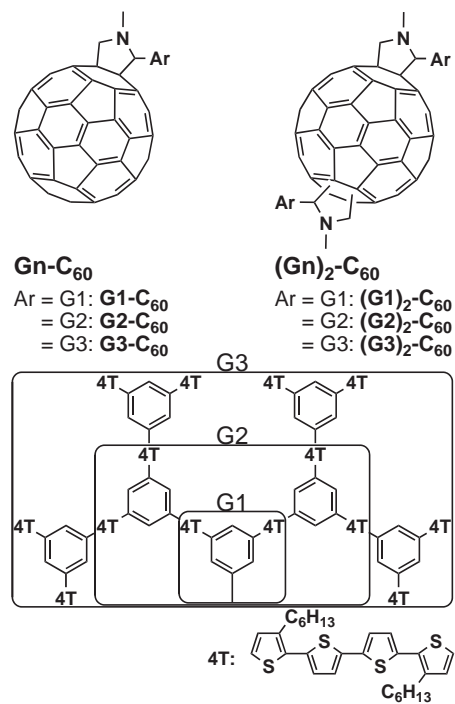   = G2: **(G2)$_2$-C$_{60}$**
   = G3: **(G3)$_2$-C$_{60}$**

Chart 1.

visible region at the nearly identical wavelengths and are assignable to π–π* transition of the 4T chromophores. Their absorption coefficients increase with increasing the number of 4T units in the molecules. In addition, weak absorptions typical of fulleropyrrolidine derivatives appeared at 700–710 nm, where the absorptions of (**G1)$_2$-C$_{60}$** and (**G2)$_2$-C$_{60}$** were slightly shifted to longer wavelengths than those of **Gn-C$_{60}$**. In the case of (**G3)$_2$-C$_{60}$**, an excessive shift of the 4T-absorption edge to near-IR region seems to conceal the weak fulleropyrrolidine absorption, suggesting that two sterically huge G3 groups partly interact with each other intramolecularly and thus cover the fullerene unit. On the other hand, compared with the corresponding **Gn-CHO**, the fluorescence of all the fullerene linkage molecules was quenched strongly (Table S1)[10] because of the occurrence of photoinduced intramolecular electron transfer from the dendritic oligothiophene to the fullerene.[12]

On cyclic voltammetry measurements (Figure S2),[10] **Gn-C$_{60}$** and (**Gn)$_2$-C$_{60}$** showed multi-step oxidation curves owing to their possessing electroactive multi-sites. Interesting features are noticed in cathodic scan. The dendritic oligothiophene/fullerene molecules except for (**G3)$_2$-C$_{60}$** revealed two reversible waves typical of fulleropyrrolidine, while no reduction peak was observed for (**G3)$_2$-C$_{60}$**, indicating that the two
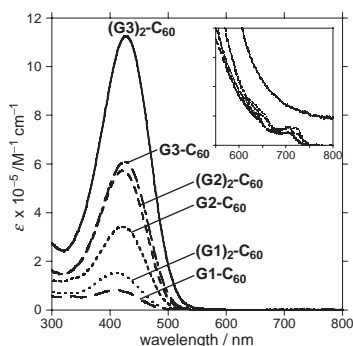
Figure 1. UV–vis absorption spectra of **G*n*-C$_{60}$** and **(G*n*)$_2$-C$_{60}$** in *o*-dichlorobenzene.

Table 1. FET mobilities of **G*n*-C$_{60}$** and **(G*n*)$_2$-C$_{60}$**

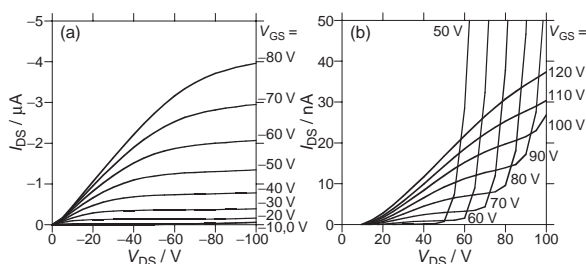| FET material	μ/cm^2 V^{-1} s^{-1}	
	Holes	Electrons
G1-C$_{60}$	7.3×10^{-7}	4.5×10^{-7}
G2-C$_{60}$	2.0×10^{-5}	7.2×10^{-8}
G3-C$_{60}$	5.4×10^{-5}	Not observed
(G1)$_2$-C$_{60}$	1.4×10^{-7}	Not observed
(G2)$_2$-C$_{60}$	1.8×10^{-5}	Not observed

Figure 2. The I_{DS} vs V_{DS} curves at different gate biases for the FET device using the thin film of **G2-C$_{60}$**: (a) hole-enhancement mode and (b) electron-enhancement mode.

bulky G3 groups completely cover the fullerene part to remarkably slow down electron transfer from the working electrode.

The bottom-contact OFET devices using the spin-coated films were fabricated and tested for both p-channel and n-channel characteristics, and they were summarized in Table 1. Typical ambipolar output was observed for the devices using **G1-C$_{60}$** and **G2-C$_{60}$**, and Figure 2 represents the performances of **G2-C$_{60}$**-based device. Although the observed mobility of electrons is rather low compared with that of the ambipolar **16T-2C$_{60}$** (4.3×10^{-5} cm^2 V^{-1} s^{-1}),[7] it is interesting to note that the weight ratio of C$_{60}$ to oligothiophene segments in **G2-C$_{60}$** is smaller than that in **16T-2C$_{60}$**. The appearance of the ambipolar character in the **G2-C$_{60}$** film is attributable to the self-aggregation property of dendritic oligothiophenes[8] to form both electron- and hole-transporting channels. For the FET devices using **G3-C$_{60}$**, **(G1)$_2$-C$_{60}$**, and **(G2)$_2$-C$_{60}$**, no n-channel characteristic was observed, whereas the enhancement of hole mobility up to 5.4×10^{-5} cm^2 V^{-1} s^{-1} of **G3-C$_{60}$** also indicates the effects of the self-aggregation. In these films the formation of the electron-transporting channel composed of the C$_{60}$ parts might

be inhibited by the sterically large dendritic oligothiophenes or by the two-dendron substitution as seen typically in the cyclic voltammogram of **(G3)$_2$-C$_{60}$**.

In conclusion, we have successfully synthesized the dendritic oligothiophene/[60]fullerene linkage molecules. The appearance of ambipolar character on the FET devices using **G1-C$_{60}$** and **G2-C$_{60}$** in spite of their small weight ratios of the fullerene segments indicates that the self-aggregation of the dendritic oligothiophene parts effectively contributes the formation of hole- as well as electron-transporting channels. We anticipate that further molecular designs based on the combination of dendritic oligothiophenes with fullerenes will develop prospective materials for ambipolar FET as well as photovoltaic devices.

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