

Fullerene-tethered oligothiophenes as advanced molecular electronics materials*

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Abstract: This article reviews the recent progress of fullerene-tethered oligothiophenes as advanced molecular electronics materials. By covalent linkage with fullerenes, oligothiophenes can be modified into intelligent functional materials. In addition to the characteristics of oligothiophenes as well as fullerenes, these linkage systems show intriguing physical properties such as photoinduced electron transfer, energy transfer, and ambipolar conductivity, caused by interactions between both components. These properties are of great use for the wide applications of the linkage compounds to devices. Their practical uses for photovoltaic cells and field effect transistors are demonstrated.

Keywords: Molecular electronics; fullerene-tethered oligothiophenes; oligothiophenes; photoinduced electron transfer; ambipolar conductivity.

INTRODUCTION

Structurally well-defined conjugated α -linked oligothiophenes have currently attracted much attention in terms of nanoarchitecture [1]. Modern synthetic techniques have allowed the development of extraordinarily long oligothiophenes such as the 48-mer [2] and the 96-mer [3]. These long oligothiophenes take *all-trans* rigid rod structures with extensive conjugation over 20–30 thiophene units, and accordingly, show unique electronic and photophysical properties, reminiscent of those of polythiophene. By further modifications of their molecular structures with electroactive or photoactive groups, they can be transformed into more intelligent systems that serve as molecular electronics materials. Along this line, our group has recently devoted its efforts to the development of functional oligothiophenes covalently linked with fullerenes. Here, we review the developments and properties of a variety of fullerene-tethered oligothiophenes and their potential as advanced molecular electronics materials, demonstrating some examples of their applications.

FULLERENE/OLIGOTHIOPHENE SYSTEMS

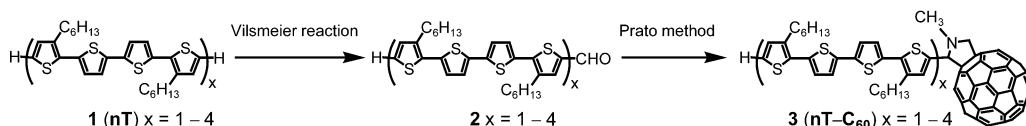
Photoinduced electron- or energy-transfer is a key function for the construction of optoelectronic devices or artificial photosynthetic systems. In our search for such promising systems, we developed a series of fullerene-linked oligothiophenes **3** (abbreviated as **nT-C₆₀**), in which [60]fullerene is covalently bonded to the terminal position of hexyl-substituted oligothiophenes **1** (**nT**) [4]. In this dyad system, it

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is expected that the oligothiophene and the fullerene can behave as a weak electron donor and a weak electron acceptor, respectively, and accordingly, both components may interact with each other in the excited states.

The syntheses of the dyads (**nT-C₆₀**) were accomplished by use of a combination of the Vilsmeier reaction of the oligothiophenes **1** and the coupling of the resulting aldehydes **2** with fullerene in the presence of *N*-methylglycine (Prato method) [5], as shown in Scheme 1.



Scheme 1 Synthesis of oligothiophene/fullerene dyads **3**.

The electronic absorption spectra of compounds **3** were explained in terms of a simple superposition of the electronic transitions of the two components. This means that there is no electronic interaction between the two components in the ground state. In contrast, the emission spectrum showed a marked interaction between both components in the excited state. The emission spectrum of **4T-C₆₀** in toluene, when the oligothiophene was selectively excited, demonstrated no appreciable fluorescence from the oligothiophene chromophore [4]. Alternative fluorescence was observed around 700 nm, being assignable to an emission from the fullerene chromophore. Evidently, in the dyad system, a fast intramolecular singlet–singlet energy transfer from the excited oligothiophene component to the fullerene occurs. On the other hand, the emission spectra of the higher homologues **8T-C₆₀** and **12T-C₆₀** showed dual fluorescence not only from the fullerene, but also from the oligothiophene as a result of the retardation of energy transfer due to an increasing separation between both component centers. However, energy transfer is still predominant.

Further detailed spectroscopic studies of **3** revealed that the photophysical decay process is solvent-dependent [6]. In polar solvents such as benzonitrile and THF, neither fluorescence from the oligothiophene nor from the fullerene was observed. This strongly suggests an intramolecular electron transfer from the oligothiophene moiety to the fullerene. The actual involvement of electron transfer was verified by the observation of the radical cation species of oligothiophene and the radical anion species of fullerene in the transient absorption spectra. It is thus considered that solvation by the polar solvent stabilizes the charge-separation state much more than the energy-transfer state, with the result that electron transfer predominantly occurs. The photophysical energy diagram for **8T-C₆₀** is illustrated in Fig. 1. Different from energy transfer, electron transfer occurs rapidly as the oligothiophene chain increases, because the lower oxidation potential of the long oligothiophene is more effective in lowering the energy level of the charge-separation state [6b].

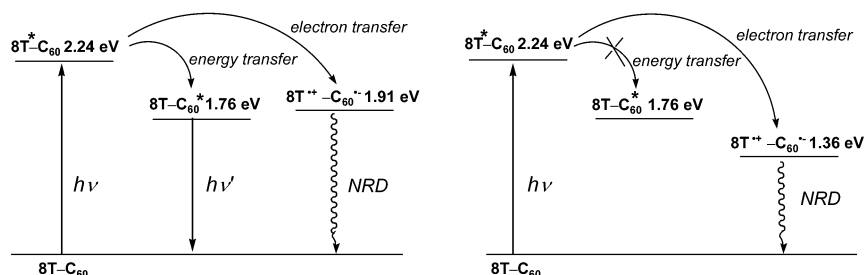
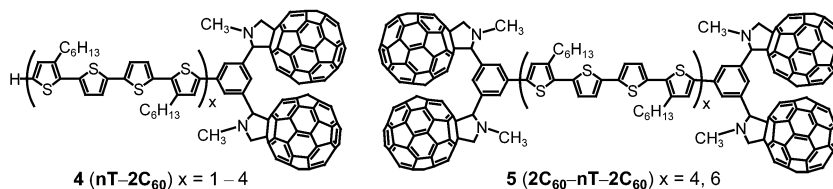
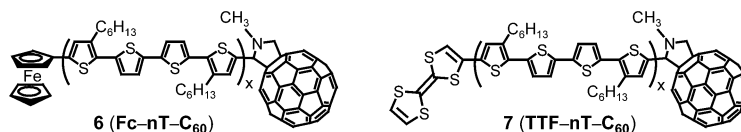


Fig. 1 Photophysical decay diagram of **8T-C₆₀**: left in toluene; right in benzonitrile.

It is expected that the increasing number of the pendant fullerenes in the present linkage system promotes intramolecular electron transfer. In this regard, we were interested in multifullerene-linked oligothiophenes **4** (**nT-2C₆₀**) [7] and **5** (**2C₆₀-nT-2C₆₀**) [8], which were also synthesized from the corresponding aldehydes using the Prato method. The modified oligothiophenes **4** and **5** also showed marked quenching of the oligothiophene emission. As expected, the quenching is much larger than that of **nT-C₆₀**. The promoted photoinduced electron transfer led to the successful development of the photovoltaic cell of **16T-2C₆₀** with the highest performance among those using fullerene-tethered oligothiophenes (vide infra).



Another promising modification of **nT-C₆₀** is extension to novel triads by additional attachment with an electron donor unit at the opposite terminal site of the oligothiophene. In this context, we studied the triads **6** (**Fc-nT-C₆₀**) and **7** (**TTF-nT-C₆₀**) [9]. The attached strong electron donors, ferrocene (Fc) and tetrathiafulvalene (TTF), can serve to promote photoinduced intramolecular electron transfer and to stabilize long-range charge-separation states.



PORPHYRIN/OLIGOTHIOPHENE/FULLERENE SYSTEMS

The high conjugation of oligothiophenes makes them promising molecular wires for photoinduced electron-transfer systems (Fig. 2). It is generally known that the efficiency of electron- or energy-transfer through a molecular wire exponentially decreases with the increasing length of the molecule, and the damping factor in the exponential is a measure of a molecular wire and is closely related with the electronic structure of the molecule. Much synthetic and theoretical research has been thus devoted to find nanomolecular systems allowing long-range electron- or energy-transfer [10]. In order to evaluate oligothiophenes as long-range molecular wires, we studied the triad system **8** (**Po-nT-C₆₀**) consisting of porphyrin, oligothiophene, and fullerene [11].

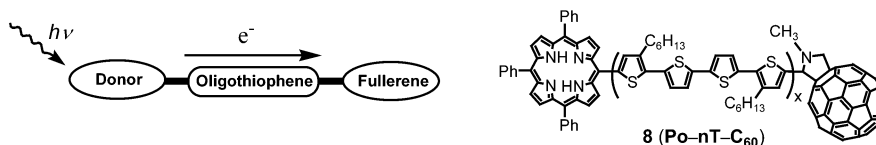


Fig. 2 Photoinduced electron-transfer system.

The electronic absorption spectrum of **Po-nT-C₆₀** measured in benzonitrile demonstrated no electronic interaction among the three components. On the other hand, the emission from the porphyrin was much quenched by addition of the opposite fullerene, and the quenching percentage depends on the chain length of the oligothiophene; 95 % for **Po-4T-C₆₀**; 46 % for **Po-8T-C₆₀**; 21 %

for **Po-12T-C₆₀**. This indicates that electron transfer considerably occurs from the porphyrin moiety to the fullerene through the oligothiophene molecule. On the basis of the quenching factors and the fluorescence lifetimes, it was calculated that the rate constants for electron-transfer reaction (k_{ET}) are $5.7 \times 10^9 \text{ s}^{-1}$ for **Po-4T-C₆₀**, $6.2 \times 10^8 \text{ s}^{-1}$ for **Po-8T-C₆₀**, and $2.0 \times 10^8 \text{ s}^{-1}$ for **Po-12T-C₆₀**. A plot of $\ln k_{ET}$ vs. the donor-acceptor distances (R_{DA}) gave a good straight line according to equation $k_{ET} = \alpha + A \exp(-\beta R_{DA})$. From the slope of the line, a damping factor $\beta = 0.11 \text{ \AA}^{-1}$ was obtained. This value for electron transfer through the oligothiophene is considerably small among those reported for other molecular wires [12]. This result shows that the oligothiophene is a superior molecular wire allowing an efficient long-range electron transfer.

With the aim to control the function of the molecular wire by an external stimulus, we further designed the porphyrin/quaterthiophene/fullerene triad **9a**, where the two central thiophenes are additionally bridged with a polyether chain [13]. As illustrated in Fig. 3, complexation of **9a** with an alkaline metal cation in the polyether chain causes a drastic conformational change to **9b**, resulting in the reduction of the conjugation of the oligothiophene segment [14]. Actually, emission from the porphyrin chromophore of **9a** was enhanced by addition of sodium perchlorate (Fig. 4), being explained as a result of depression of intramolecular electron transfer through the oligothiophene by complexation. Evidently, the polyether-bridged oligothiophene in **9a** possesses the function of a gated molecular wire, responding to complexation and decomplexation.

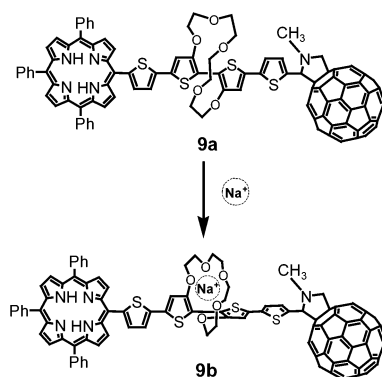


Fig. 3 A conformational change of **9a** to **9b** upon complexation with sodium cation.

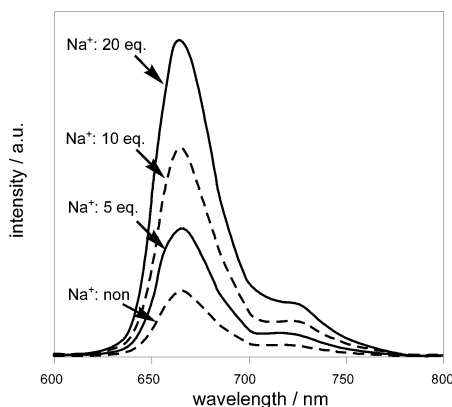


Fig. 4 Enhanced porphyrin emission of **9** in benzonitrile by addition of sodium perchlorate.

FULLERENE-LINKED OLIGOTHIOPHENES AS PHOTOVOLTAIC MATERIALS

Efficient photoinduced electron transfer from a conjugated polymer to a fullerene has paved the way to the development of efficient low-cost plastic solar cells [15]. Early devices containing both components in a bilayer type yielded only low performance for solar power conversion, but modified devices using a blend of both components in the organic layer achieved considerable improvement; the recent power conversion efficiency of the best class reaches to a few percents. Nevertheless, organic solar cells are still far inferior to conventional silicon-based solar cells. Presumably, the low performance of the former is partly because of low probability of intermolecular electron transfer between the two components due to insufficient interface area. In expectation of the high probability of intramolecular electron transfer, the fullerene-containing polymers [16] and oligomers [17] were recently developed. However, the efficiency of such devices has been limited by competition between photoinduced electron transfer and energy transfer from the donor component to the fullerene. The discovery of highly efficient photoinduced electron transfer for **nT-C₆₀** in solid state [18] prompted us to investigate its application to photovoltaic cells [19]. The sandwich device of Al/**nT-C₆₀**/Au was fabricated, as depicted in Fig. 5, where the semitransparent Al film was first vacuum-deposited on a glass substrate, the organic film was spin-coated from a chloroform solution, and finally, the Au-film cover electrode was vacuum-deposited. Under illumination from the Al side with a 10 $\mu\text{W}/\text{cm}^2$ tungsten-halogen lamp attached to a monochromator, the device showed a marked photocurrent (Fig. 6). The action spectrum was in accordance with the absorption spectrum of the oligothiophene chromophore.

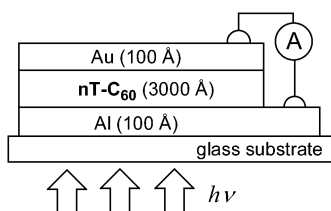


Fig. 5 Schematic structure of the photovoltaic cell of **nT-C₆₀**.

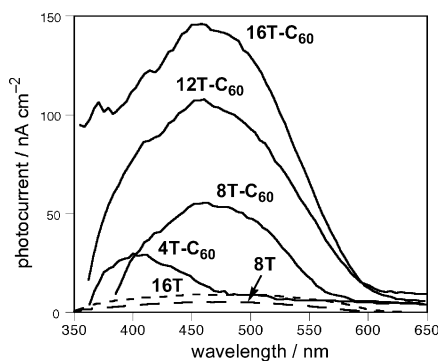


Fig. 6 Photocurrents of photovoltaic cells.

Table 1 summarizes the short circuit currents (I_{sc}), the incident light wavelengths (λ_{inc}), and the incident photon to converted electron efficiency (IPCE) at maximum photocurrents of the photovoltaic cells based on several fullerene-linked oligothiophenes. The generated photocurrent is larger by one order in magnitude than that using the unmodified oligothiophene **1** and remarkably depends on the oligothiophene length. It is thus evident that the intramolecular electron transfer of the dyad system contributes to the generation of large photocurrent, and the long oligothiophene component greatly con-

tributes to the construction of an efficient network for hole transportation through intermolecular interactions, as illustrated in Fig. 7.

Table 1 Photovoltaic performances of the sandwich cells.

Organic film	$I_{SC}/nA\text{ cm}^{-2}$	λ_{inc}/nm	IPCE/%
4T-C ₆₀	30	410	2.1
8T-C ₆₀	56	459	3.7
12T-C ₆₀	108	461	7.0
16T-C ₆₀	148	456	9.7
12T-2C ₆₀	210	460	14
16T-2C ₆₀	376	466	25
2C ₆₀ -24T-2C ₆₀	210	463	14

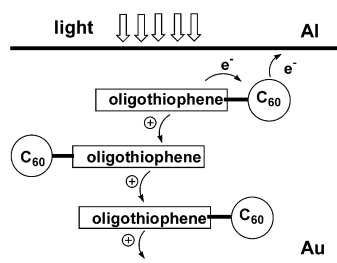


Fig. 7 Schematic mechanism for the generation of photocurrent.

The multifullerene-linked systems **nT-2C₆₀** and **2C₆₀-nT-2C₆₀** also demonstrated marked photovoltaic performances (see also Table 1). The photocurrents of the cells with **12T-2C₆₀** and **16T-2C₆₀** are nearly double or more of those with **12T-C₆₀** and **16T-C₆₀** [7]. This is because an increase of the pendant fullerenes promotes photoinduced charge separation and strengthens intermolecular electronic interactions among the fullerenes, constituting a considerably efficient network for electron transport. As an exception, the photocurrent of the **2C₆₀-24T-2C₆₀** cell is the same as that with **12T-2C₆₀** and rather less than that with **16T-2C₆₀** [8]. This is ascribable to roughness for the surface morphology of the **2C₆₀-24T-2C₆₀** film, as evidenced by the AFM image of the **2C₆₀-24T-2C₆₀** film.

FULLERENE-LINKED OLIGOTHIOPHENES AS AMBIPOLAR FIELD-EFFECT TRANSISTOR MATERIALS

Field-effect transistors (FETs) based on one kind of organic materials are currently receiving significant attention in terms of easy processing and low cost. In particular, ambipolar FETs that show both *p*-type and *n*-type semiconductivities depending on the positive or negative sign of the gate bias are of special interest, but still limited. Only two examples of ambipolar organic semiconductors were very recently reported [20]. The large photocurrent generation of the photovoltaic cells based on fullerene-linked oligothiophenes is clearly ascribed not only to the efficient photoinduced electron transfer, but also to marked hole and electron migration in the thin film. This means that these compounds also have high potentials as active ambipolar conductors. We then explored the transistor performances of the fullerene-linked oligothiophenes by fabricating a bottom-contact type of FET device (Fig. 8). The device using **16T-C₆₀** demonstrated a FET response only in hole-enhancement mode [21]. On the other hand, the device using **16T-2C₆₀** operated in both hole- and electron-enhancement modes, thanks to the improved network for electron transport. Figure 9 shows the drain-source current (I_{ds}) characteristics with different gate voltage (V_g) for this device. At negative low V_g and negative high V_{ds} , I_{ds} in-

creased with an increase of V_{ds} (Fig. 9a), which is characteristic of an ambipolar transistor. A similar steep increase of I_{ds} at low V_g was also observed in an electron-enhancement mode (Fig. 9b). The field effect mobilities are $1.1 \times 10^{-5} \text{ cm}^2/\text{V s}$ for hole transport and $4.3 \times 10^{-5} \text{ cm}^2/\text{V s}$ for electron transport. Finally, it is emphasized that, to the best of our knowledge, **16T-2C₆₀** is the third ambipolar organic semiconductor.

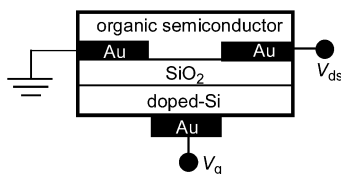


Fig. 8 Schematic illustration of the FET device.

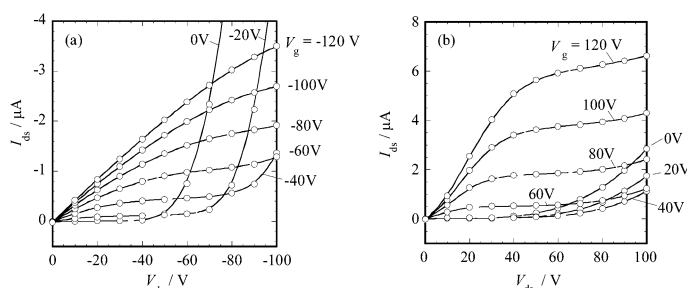


Fig. 9 I_{ds} vs. V_{ds} curves at different gate biases for the FET device of the **16T-2C₆₀** thin film. The ambipolar transistor operating in (a) hole-enhancement and (b) electron-enhancement mode.

CONCLUDING REMARKS

Functional oligothiophenes are very promising as advanced molecular electronics materials. In this context, we have demonstrated here that fullerene-tethered oligothiophenes can be obtained with high purity levels (electronic grade) by conventional synthetic methods and can be easily converted into molecular kits that are advantageous to nanoarchitecture. In addition, it has turned out that they have many intriguing physical properties meeting the requirements of molecular electronics materials. In fact, they have been successfully applied to the fabrication of photovoltaic devices and FET devices. Furthermore, the photophysical studies of the porphyrin/oligothiophene/fullerene system as well as other triad systems have revealed that the oligothiophene can behave as a long-range molecular wire, and also that such triad systems can constitute photoinduced long-range charge-separation states. It is thus evident that fullerene-tethered oligothiophenes are prototypical molecular systems that could find versatile uses in a number of devices.

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