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Oligothiophene-multifullerene linkage molecules as high performance photovoltaic materials

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Abstract

Novel long oligothiophenes incorporated with four fullerenes (**$2C_{60}$–16T–$2C_{60}$** and **$2C_{60}$–24T–$2C_{60}$**) have been synthesized with the aim of developing good single-component photovoltaic materials. The tetracosithiophene derivative **$2C_{60}$–24T–$2C_{60}$**, despite its giant structure, is rather more tractable regarding solubility than the hexadecithiophene derivative **$2C_{60}$–16T–$2C_{60}$**. The electronic absorption and emission spectra of **$2C_{60}$–24T–$2C_{60}$** indicated no electronic interaction in the ground state but efficient intramolecular electron transfer in the excited state. The sandwich device of the Al/**$2C_{60}$–24T–$2C_{60}$**/Au structure showed a marked photocurrent upon illumination with monochromatic light from the Al side. The incident-photon to converted-electron ratio (IPCE) is 14%.

Keywords: polythiophene and derivative, fullerenes and derivatives, solar cells, amorphous thin films, photoconductivity

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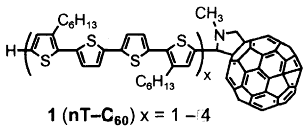
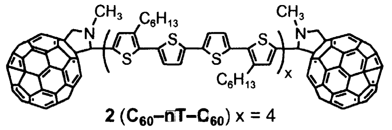
1. Introduction

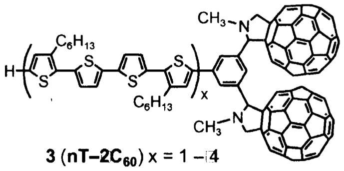
Conjugated oligomers incorporated with fullerenes are expected to be promising materials for organic solar cells [1]. As a prototype of such materials, we have recently focused on the oligothiophene-fullerene dyads **1** (abbreviated as **nT–C_{60}** depending on the number of the thiophene units), which can induce highly efficient photoinduced charge separation [2]. Actually, these dyads formed good single-component films for a sandwich type of photovoltaic cells [3]. The performance of the photovoltaic cells markedly increases with the chain extension of oligothiophenes. Specifically, the Al/**16T–C_{60}**/Au cell showed appreciably high power conversion efficiency (0.40 %) upon illumination from the Al side with light of 456 nm. However, it was also revealed that similar illumination from the Au side generated only a half of the photocurrent. This suggests that charge carriers formed in the neighborhood of the Al side mainly contribute to the generation of the photocurrent. In other words, the long-oligothiophene components of the dyads



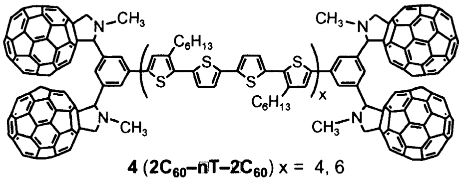
1 (**nT–C_{60}**) x = 1 – 4



2 (**C_{60}–nT–C_{60}**) x = 4



3 (**nT–$2C_{60}$**) x = 1 – 4



4 (**$2C_{60}$–nT–$2C_{60}$**) x = 4, 6

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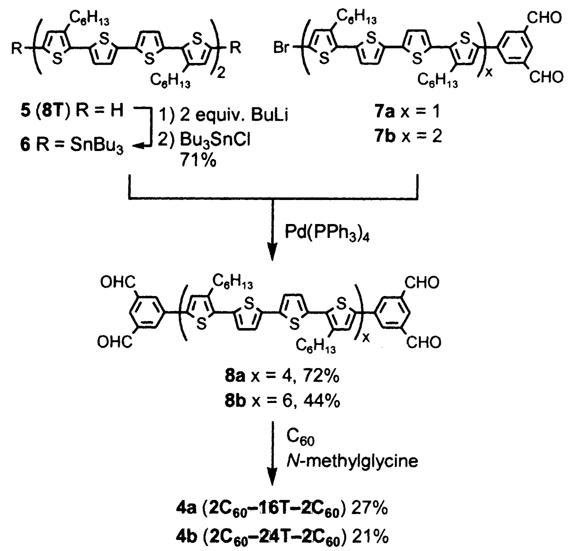
constitute an efficient network for hole transport in a film of molecular assembly, while the fullerene components do not interact with each other enough to promote electron transport. That is, the performance of the devices based on **nT–C$_{60}$** is considerably limited due to the insufficient relay of electron transport among fullerenes.

Concerning the enhancement of electron transporting abilities, we considered that increasing the number of the pendant fullerenes in the linkage system would strengthen intermolecular interactions among the fullerenes, and accordingly, make a good path for electron transfer. We then focused on the triads **2** (**C$_{60}$–nT–C$_{60}$**) and **3** (**nT–2C$_{60}$**) composed of one oligothiophene and two fullerenes [4]. However, the triad **2** (**C$_{60}$–16T–C$_{60}$**), where two fullerenes are incorporated at the opposite terminals of hexadecithiophene, is sparingly soluble in common solvents owing to its symmetrical structure and intractable nature. On the other hand, the unsymmetrical triads **3**, where two fullerenes are incorporated at the same terminal of oligothiophenes, are soluble enough to be spin-coated, providing good films. The sandwich devices of **12T–2C$_{60}$** and **16T–2C$_{60}$** demonstrated markedly improved photovoltaic performance: the monochromic power conversion efficiency of the Al/**12T–2C$_{60}$**/Au cell is 0.50% and that of the Al/**16T–2C$_{60}$**/Au cell 0.64%. There is thus no doubt that increasing the number of the pendant fullerenes serves to improve a relay network for electron transfer, and the oligothiophene-multifullerene linkage molecules show great potential as high-performance photovoltaic materials. As our further effort directed toward the development of novel oligothiophene-multifullerene linkage molecules, we report herein the synthesis, spectroscopic properties, and photovoltaic characteristics of the pentads **4** (**2C$_{60}$–nT–2C$_{60}$**), where two pendant fullerenes are incorporated at each terminal of long oligothiophenes (n = 16, 24).

2. Results and Discussion

Scheme 1 outlines a synthetic route of the two pentads **4a** (**2C$_{60}$-16T-2C$_{60}$**) and **4b** (**2C$_{60}$-24T-2C$_{60}$**). First, the tetrahexyl-substituted octithiophene **5** (**8T**) [5] was treated with butyllithium in tetrahydrofuran at –50 °C, followed by tributyltin chloride at room temperature to give the bis(tributylstannyl)octithiophene derivative **6** in 71% yield. The Stille coupling of **6** with two equivalents of the bromo-quaterthienyl-benzenedialdehyde **7a**, a key intermediate in the synthesis of **nT-2C$_{60}$** [4], in refluxing toluene containing a catalytic amount of tetrakis(triphenylphosphine) palladium(0) produced the hexadecithiophene-bis(benzenedialdehyde) **8a** in 72% yield. A similar coupling reaction between **6** and two equivalents of the bromo-octithienyl-benzenedialdehyde **7b** [4] gave the tetracosithiophene derivative **8b** in 44% yield. Finally, the aldehydes **8a** and **8b** thus obtained were treated with [60]fullerene and *N*-methylglycine in *o*-dichlorobenzene at 140 °C according to the Prato method [6] to smoothly afford the corresponding pentads **4a** (27% yield) and **4b** (21% yield).

Scheme 1



The unknown pentads **4** and intermediates **8** were satisfactorily characterized by spectroscopic measurements and elemental analyses [7]. Considering the symmetrical structure as well as the chain extension of oligothiophene and the increasing number of fullerenes, we were anxious about the solubility problem of pentads **4** when we started this project. Certainly, the pentads **4** are less soluble in common solvents than the unsymmetrical triads **3**. However, it turned out that, surprisingly, the longer **4b** has better solubility than the short **4a**. The insolubility of the lower homologues in this pentad series led to failure of our attempted synthesis of the octithiophene derivative **4** (x = 2). These results are in sharp contrast to a general trend that the solubility of oligothiophenes drastically decreases with the chain extension.

Figure 1 shows the electronic absorption and emission spectra of **2C$_{60}$–24T–2C$_{60}$** in *o*-dichlorobenzene. The absorption spectrum is featured by two strong bands at 319 nm (ε 186,000) and 477 nm (ε 193,000) tailing up to 700 nm. This is understood to be a superimposition of absorption bands due to the oligothiophene and fullerene chromophores. The striking band at 477 nm is due to the oligothiophene, and the strong short-wavelength band at 319 nm as well as the weak long-wavelength band tailed to 700 nm due to the fullerene. Apparently, there is no interaction between both chromophores in the ground state. On the other hand, the emission spectrum is characterized by marked reduction of the oligothiophene fluorescence, when the oligothiophene chromophore is excited. The intensity is less than 1% as compared to the strong emission of long oligothiophenes. This indicates that in the photoexcited state, the electron transfer of the oligothiophene chromophore to the pendant fullerene efficiently occurs, as already observed for the spectra of **nT–C$_{60}$** and **nT–2C$_{60}$**. The other pentad **2C$_{60}$–16T–2C$_{60}$** also exhibited a similar absorption spectrum, but its poor