Synthesis and Photovoltaic Effects of Oligothiophenes Incorporated with Two [60]Fullerenes

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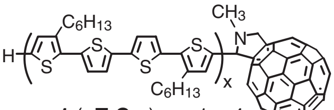
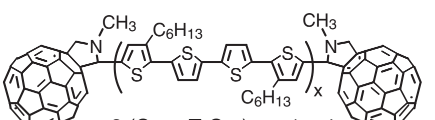
The triads (**nT-2C$_{60}$**) consisting of one oligothiophene and two fullerenes have been synthesized as single-component materials for photovoltaic cells. The sandwich-type cells of a configuration Al/**nT-2C$_{60}$**/Au generate much higher photocurrents than those based on the oligothiophene-fullerene dyads (**nT-C$_{60}$**).

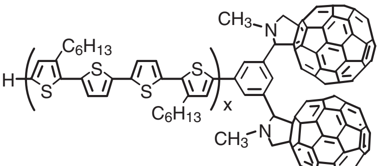
Conjugated oligomers incorporated with fullerene are expected to be promising materials for growing organic solar cells.[1,2] In this regard, we recently discovered that the oligothiophene–fullerene dyads **1** (abbreviated as **nT-C$_{60}$**) can induce highly efficient photoinduced charge separation[2] and serve as single-component materials for photovoltaic cells.[3] Specifically, the Al/**16T-C$_{60}$**/Au cell showed appreciably high power conversion efficiency (0.32%) upon illumination from the Al side with a light of 456 nm. However, illumination from the Au side generated only a half of the photocurrent at the same wavelength. This suggests that charge carriers generated close to the Al side mainly contribute to the photocurrent. In other words, the oligothiophene moiety constitutes an efficient network for hole transport in the film, while the fullerenes do not interact with one another enough to promote electron transport. We have expected that an increase of the number of fullerenes in the linkage system would enhance intermolecular interactions among the fullerenes. The fullerene–oligothiophene–fullerene triads **2** (**C$_{60}$-nT-C$_{60}$**), however, gave no good films because of their poor solubilities. We have then focused on another type of triads **3** (**nT-2C$_{60}$**), where two fullerenes are incorporated at the same terminal of oligothiophenes. Here we report the synthesis and photovoltaic properties of **nT-2C$_{60}$** ($n = 4, 8, 12, 16$).



1 (**nT-C$_{60}$**) x = 1 – 4

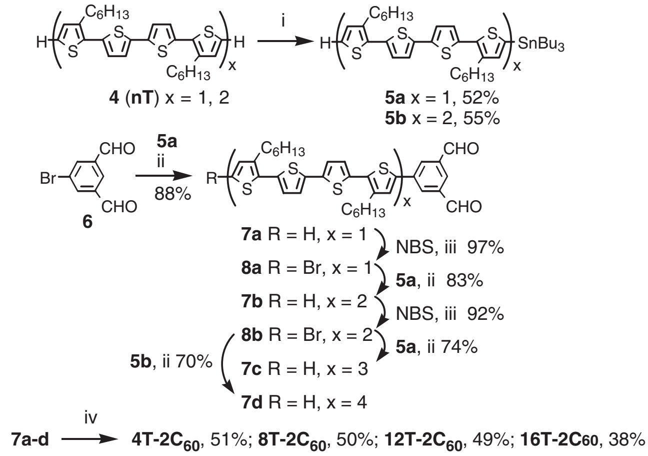


2 (**C$_{60}$-nT-C$_{60}$**) x = 1 – 4



3 (**nT-2C$_{60}$**) x = 1 – 4

Scheme 1 outlines the synthetic route of a homologous series of the triads **nT-2C$_{60}$**. The key precursors are the oligothienylbenzene-dicarbaldehydes **7a**-**7d**, which were prepared from oligothiophenes **4** (**nT**)[4] by a combination of Stille coupling reactions and bromination with NBS. The dialdehydes **7a**-**7d** thus obtained were treated with [60]fullerene and *N*-methylglycine according to Prato's method[5] to smoothly afford the corresponding triads **nT-2C$_{60}$**.[6]



Scheme 1. Reagents and conditions: i) 1 equiv. *n*-BuLi, THF, −30 °C, 0.5 h, then *n*-Bu$_3$SnCl, rt, 12 h; ii) cat. Pd(PPh$_3$)$_4$, toluene, reflux, 12 h; iii) 1 equiv. NBS, DMF-CS$_2$, rt, 15 h; iv) C$_{60}$, *N*-methylglycine, chlorobenzene, reflux, 1 d.

The electronic absorption spectra of **nT-2C$_{60}$** in *o*-dichlorobenzene consist of a superposition of a strong band of the oligothiophene chromophore at 400–600 nm and a strong band of the fullerene at around 330 nm tailing up to 700 nm (Figure 1). Apparently, there is no interaction between the two chromophores in the ground state. On the other hand, the fluorescence spectra showed marked reduction of the oligothiophene emission compared to the corresponding oligothiophene (**nT**), when the oligothiophene chromophore was excited. This indicates efficient intramolecular electron transfer from the photoexcited oligothiophene moiety to the pendant fullerene, as observed for the dyads **nT-C$_{60}$**.[2] In addition, it is worth noting that thanks to the increased number of the pendant fullerenes, the triads **nT-2C$_{60}$** undergo stronger quenching than **nT-C$_{60}$**.

The sandwich devices of Al/**nT-2C$_{60}$**/Au were fabricated as follows. A semitransparent Al electrode (100 Å) was first vacuum-deposited on a glass substrate. Then a thin film of **nT-2C$_{60}$** (2500–3000 Å) was prepared by spin-coating of a chloroform solution. Finally a Au electrode (100 Å) was vacuum-deposited. Upon illumination from the Al side with 10-µWcm^{-2} monochromatic light, the photovoltaic cells of **12T-2C$_{60}$** and **16T-2C$_{60}$** showed marked photocurrents. The action spectra are in strict accordance with the absorption spectra of the oligothiophene

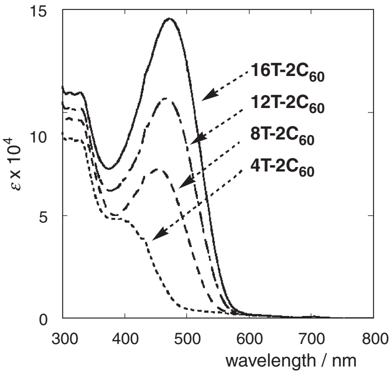


Figure 1. Electronic absorption spectra of **nT-2C$_{60}$** in *o*-dichlorobenzene.

chromophores (Figure 2). The photocurrents increase with the chain extension of the oligothiophene, similar to the case of the **nT-C$_{60}$** series. The cells of **4T-2C$_{60}$** and **8T-2C$_{60}$** showed no photocurrents, being attributable to appreciable defects in their spin-coated films.

The maximum short-circuit photocurrent (I_{SC}) of the Al/**12T-2C$_{60}$**/Au cell is 210 nA·cm^{-2} at 460 nm, and that of the Al/**16T-2C$_{60}$**/Au is 376 nA·cm^{-2} at 466 nm. These values correspond to the incident photon to converted electron ratios (IPCE) of 14% for **12T-2C$_{60}$** and 25% for **16T-2C$_{60}$**, which are nearly double of those previously measured using **nT-C$_{60}$** (Table 1). This result evidently indicates that the triads **nT-2C$_{60}$** constitute the improved fullerene network for electron transport. It was found that the monochromatic power conversion efficiency is reasonably high: 0.50% for the Al/**12T-2C$_{60}$**/Au cell and 0.65% for the Al/**16T-2C$_{60}$**/Au.

In conclusion, we have developed the triads **nT-2C$_{60}$** as novel single-component photovoltaic materials. It has turned out that these triads constitute an improved network for electron transport owing to the increased number of the pendant fullerenes, as compared to the previous dyads **nT-C$_{60}$**.

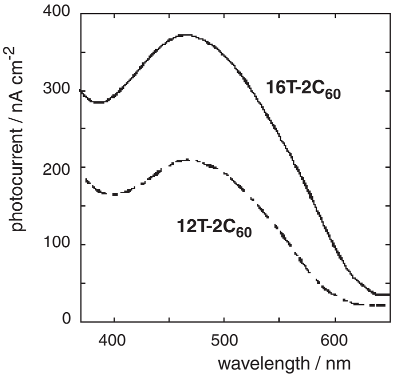


Figure 2. Photocurrent action spectra of the Al/**nT-2C$_{60}$**/Au cells.

Table 1. Photovoltaic properties of **nT-2C$_{60}$** and **nT-C$_{60}$**

Comp.	I_{SC}/nAcm^{-2}	λ_{inc}/nm	IPCE/%	V_{OC}/V	FF	η/%
12T-2C$_{60}$	210	460	14	0.66	0.36	0.50
16T-2C$_{60}$	376	466	25	0.58	0.30	0.65
12T-C$_{60}$	108	461	7.0			
16T-C$_{60}$	148	456	9.7	0.64	0.34	0.32

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6 All new compounds were satisfactorily characterized by spectroscopic measurements and elemental analyses. The triads **nT-2C$_{60}$** are a 1:1 mixture of two diasteromers originated from chiral substitution on the pyrroridine rings. Selective properties of **4T-2C$_{60}$**: brown powder from 1:9 carbon disulfide–hexane; mp > 300 °C; ^{1}H NMR (CDCl$_3$/CS$_2$) δ 0.84–0.88 (m, 12H), 1.25–1.34 (m, 24H), 1.58–1.69 (m, 8H), 2.50 and 2.65 (each br, 6H, isomeric), 2.71–2.78 (m, 8H), 4.23 and 4.26 (each d, $J = 10$ Hz, 2H, isomeric), 4.94–5.00 (m, 8H), 6.87 (d, $J = 5.3$ Hz, 2H), 6.94 (d, $J = 3.8$ Hz, 1H), 6.94 (d, $J = 3.8$ Hz, 1H), 6.97 (d, $J = 3.8$ Hz, 1H), 7.00 (d, $J = 3.8$ Hz, 1H), 7.04 (d, $J = 3.8$ Hz, 2H), 7.06 (d, $J = 3.8$ Hz, 1H), 7.06 (d, $J = 3.8$ Hz, 1H), 7.11 (d, $J =$ 5.3 Hz, 2H), 7.12 and 7.15 (each s, 1H, isomeric), 7.74 (br, 2H); MS (MALDI-TOF) m/z 2124.8 (M$^+$, calcd 2126.3). **8T-2C$_{60}$**: brown powder from 1:9 carbon disulfide–hexane; mp 220 °C (dec.); ^{1}H NMR (CDCl$_3$/CS$_2$) δ 0.87–0.92 (m, 24H), 1.26–1.42 (m, 48H), 1.62–1.68 (m, 16H), 2.50 and 2.66 (each br, 6H, isomeric), 2.71–2.78 (m, 16H), 4.24 and 4.26 (each d, $J = 8$ Hz, 2H, isomeric), 4.95–5.00 (m, 8H), 6.90 (d, $J = 5.2$ Hz, 2H), 6.95 (s, 4H), 6.98 (d, $J = 3.8$ Hz, 3H), 7.00 (d, $J = 3.8$ Hz, 4H), 7.02 (d, $J = 3.8$ Hz, 1H), 7.07 (d, $J = 3.8$ Hz, 3H), 7.08 (d, $J = 3.8$ Hz, 5H), 7.13 (d, $J = 5.2$ Hz, 2H), 7.15 and 7.18 (s, 1H, isomeric), 7.74 (br, 2H); MS (MALDI-TOF) m/z 2622.5 (M$^+$, calcd 2622.4). **12T-2C$_{60}$**: brick red powder from 1:9 carbon disulfide–hexane; mp 180 °C (dec.); ^{1}H NMR (CDCl$_3$/CS$_2$) δ 0.85–0.93 (m, 36H), 1.31–1.40 (m, 72H), 1.60–1.72 (m, 24H), 2.51 and 2.68 (each br, 6H, isomeric), 2.73–2.78 (m, 24H), 4.24 and 4.26 (each d, $J =$ 9 Hz, 2H, isomeric), 4.94–5.01 (m, 8H), 6.89 (d, $J = 5.1$ Hz, 2H), 6.94 (s, 4H), 6.95 (s, 4H), 6.97 (d, $J = 3.8$ Hz, 3H), 6.98–7.00 (m, 8H), 7.02 (d, $J = 3.8$ Hz, 1H), 7.06 (d, $J = 3.8$ Hz, 3H), 7.08 (d, $J =$ 3.8 Hz, 5H), 7.09 (d, $J = 3.8$ Hz, 4H), 7.13 (d, $J = 5.1$ Hz, 2H), 7.14 and 7.17 (s, 1H, isomeric), 7.74 (br, 2H); MS (MALDI-TOF) m/z 3119.8 (M$^+$, calcd 3119.6). **16T-2C$_{60}$**: brick red powder from 1:9 carbon disulfide–hexane; mp 160 °C (dec.); ^{1}H NMR (CDCl$_3$/CS$_2$) δ 0.86–0.93 (m, 48H), 1.26–1.42 (m, 96H), 1.60–1.70 (m, 32H), 2.49 and 2.86 (each br, 6H, isomeric), 2.74–2.78 (m, 32H), 4.24 and 4.26 (each d, $J = 9$ Hz, 2H, isomeric), 4.93–5.00 (m, 8H), 6.90 (d, $J = 5.1$ Hz, 2H), 6.95 (s, 4H), 6.96 (s, 8H), 6.98 (d, $J = 3.8$ Hz, 3H), 6.99 (d, $J = 3.8$ Hz, 1H), 7.00 (d, $J = 3.8$ Hz, 1H), 7.00 (d, $J = 3.8$ Hz, 5H), 7.01 (d, $J = 3.8$ Hz, 5H), 7.02 (d, $J = 3.8$ Hz, 1H), 7.07 (d, $J = 3.8$ Hz, 3H), 7.08–7.10 (m, 13H), 7.13 (d, $J = 5.1$ Hz, 2H), 7.14 and 7.17 (each s, 1H, isomeric), 7.45 (br, 2H); MS (MALDI-TOF) m/z 3614.8 (M$^+$, calcd 3615.7).