Synthesis and Photovoltaic Properties of Tetrathiafulvalene–Oligothiophene–Fullerene Triads

Hiroki Kanato, Masashi Narutaki, Kazuo Takimiya, Tetsuo Otsubo,* and Yutaka Harima
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
Higashi-Hiroshima 739-8527

(Received March 24, 2006; CL-060360; E-mail: otsubo@hiroshima-u.ac.jp)

Novel tetrathiafulvalene–oligothiophene–fullerene triads have been synthesized as single-component materials for photovoltaic cells. They showed somewhat improved photovoltaic performances, when compared to the corresponding oligothiophene–fullerene dyads.

Conjugated oligomers incorporated with fullerene are promising single-component materials for organic solar cells.[1] Actually, we observed high photovoltaic performances for oligothiophene–fullerene dyads (**1**, abbreviated as **nT–C$_{60}$**),[2] which were initiated by efficient photoinduced charge separation between both components.[3] In order to further promote this photoinduced charge separation, we have intended to study the tetrathiafulvalene–oligothiophene–fullerene triads (**2**, **TTF–nT–C$_{60}$**) with additional attachment of TTF at the unsubstituted terminal site of the oligothiophene. TTF is a strong electron donor to form a wide number of highly conductive molecular complexes.[4] Therefore, the **TTF–nT–C$_{60}$** triads are expected to induce long-distance charge separation and behave as good single-component materials for photovoltaic cells. Here, we report the synthesis and photophysical properties of **2a**–**2c** ($x = 1$–3), in comparison with the **nT–C$_{60}$** dyads **1a**–**1c** and the **TTF–nT** dyads **3a** and **3b** (Chart 1).

Scheme 1 outlines the synthetic route of a series of the triads **2a**–**2c**. First, oligothiophenes **4a**–**4c** were converted into the corresponding bromooligothiophenecarbaldehydes **5a**–**5c** by a combination of the Vilsmeier formylation and bromination with NBS.[5] The subsequent Stille coupling reactions between **5a**–**5c** and tributylstannyltetrathiafulvalene[6] gave the TTF-linked oligothiophenecarbaldehydes **6a**–**6c**, which were then treated with [60]fullerene and *N*-methylglycine according to the Prato protocol[7] to smoothly afford the desired triads **2a**–**2c**.[8] TTF–oligothiophene dyads **3a** and **3b** were prepared by the Stille coupling between tributylstannyltetrathiafulvalene and bromooligothiophenes **7a** and **7b** obtained by NBS bromination of **4a** and **4b**.[5]

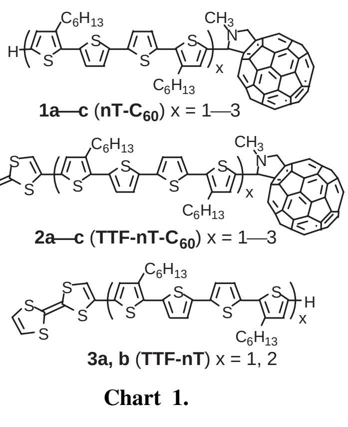
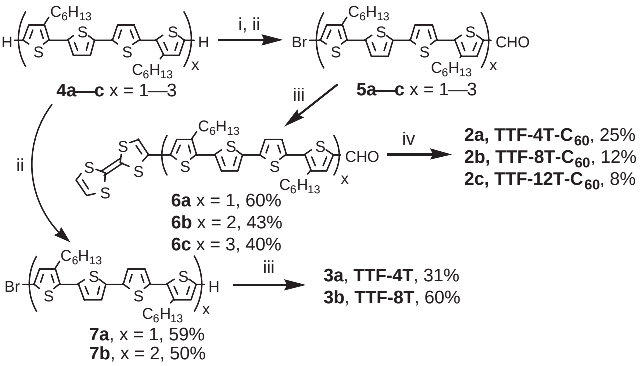


Chart 1.



Scheme 1. Reagents and conditions: i) DMF, POCl$_3$, ClCH$_2$CH$_2$Cl, 40 °C, 12 h; ii) NBS, CS$_2$–DMF, rt, 12 h; iii) tributylstannyltetrathiafulvalene, cat. Pd(PPh$_3$)$_4$, toluene, reflux, 2 h; iv) fullerene, *N*-methylglycine, chlorobenzene, reflux, 1 d.

The cyclic voltammograms of the **TTF–nT–C$_{60}$** triads demonstrated multi-oxidation waves due to the TTF and oligothiophene components in the anodic region and one reduction wave due to the fullerene component in the cathodic region. The half-wave redox potentials are summarized in Table 1, together with those of **nT–C$_{60}$** and **TTF–nT**.

Considering the half-wave oxidation potential (+0.35 and +0.80 V vs Ag/AgCl) of TTF, the first and second oxidation waves of the triads **2a** and **2b** as well as the dyads **3a** and **3b** can be assigned to be due to the TTF component. The following oxidation waves are attributable to the oligothiophene component. In the case of **2c**, the second oxidation wave of the TTF component overlaps with the oxidation wave of the dodecithiophene component. Considering that the attached TTF component in the triads **2a**–**2c** has a lower oxidation potential than the oligothiophene component, one may expect an electron transfer

Table 1. Half-wave redox potentials and electronic absorption data of **1a**–**1c**, **2a**–**2c**, and **3a** and **3b**

Comp.	$E_{1/2}$/V[a]	$\lambda_{\max}$ (log ε)[b]
1a	+0.92 (4T), −0.59 (C$_{60}$)	384 (4.44)
1b	+0.69 (8T), −0.59 (C$_{60}$)	450 (4.78)
1c	+0.59 (12T), −0.59 (C$_{60}$)	463 (4.99)
2a	+0.41, +0.82 (TTF), +1.03 (4T), −0.59 (C$_{60}$)	406 (4.61), 326 (4.71), 702 (2.30)
2b	+0.41, +0.74 (TTF), +0.89 (8T), −0.59 (C$_{60}$)	458 (4.84), 329 (4.76), 701 (2.87)
2c	+0.40 (TTF), +0.61 (TTF, 12T), −0.59 (C$_{60}$)	470 (5.00), 328 (4.78), 702 (3.24)
3a	+0.41, +0.84 (TTF), +0.97 (4T)	405 (4.46)
3b	+0.40, +0.73 (TTF), +0.82 (8T)	457 (4.83)

[a]Measurement conditions: solvent, benzonitrile; supporting electrolyte, 0.1 M *n*-Bu$_4$NPF$_6$; working electrode, Pt wire; counter electrode, Pt wire; reference electrode, Ag/AgCl; scan rate, 100 mV/s. [b]Measured in benzonitrile.

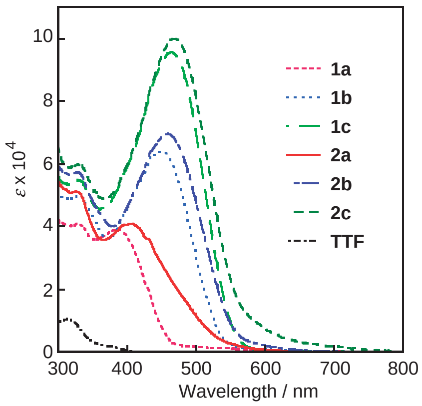


Figure 1. Electronic absorption spectra of **1a**–**1c**, **2a**–**2c**, and TTF in benzonitrile.

from the TTF component to the photoexcited oligothiophene.

Figure 1 demonstrates the electronic absorption spectra of **TTF–nT–C$_{60}$** in benzonitrile. As a whole, these spectra are explained as overlapping of the absorption bands due to the three chromophores characterized by a strong π–π^* band of oligothiophene at 400–500 nm and a strong band of fullerene at around 330 nm tailing up to 700 nm. TTF itself has a weak long-wavelength band at λ_{max} 448 nm (log ε 2.41), but in the spectra of **2a**–**2c**, it is concealed by the strong band of oligothiophene. When compared to those of the dyads **1a**–**1c**, the absorption maxima due to the respective oligothiophenes of **2a**–**2c**, and **3a** and **3b** are red-shifted by 7–22 nm, indicating some electronic interactions between the oligothiophene and TTF chromophores (see also Table 1).

In the emission spectra in benzonitrile, the **TTF–nT–C$_{60}$** triads exhibited inappreciable emission either from the photoexcited oligothiophene or from the photoexcited fullerene. Evidently, intramolecular electron transfer entirely dominates the photophysical decay process. It was already revealed that the emission spectra of the **nT–C$_{60}$** dyads are efficiently quenched by photoinduced intramolecular electron transfer from the oligothiophene to the fullerene.[3] The emission spectra of the **TTF–4T** and **TTF–8T** dyads in benzonitrile showed marked reduction of the oligothiophene emission by one order of magnitude compared to the corresponding oligothiophene (**nT**). These results suggest that efficient intramolecular electron transfer among the three chromophores may occur to long-range charge separation to **TTF$^{\bullet+}$–nT–C$_{60}$$^{\bullet-}$**.[9]

In order to examine the potential of the triads **3a**–**3c** as single-component materials for photovoltaic cells, their sandwich devices with a configuration structure Al/**TTF–nT–C$_{60}$**/Au were fabricated in the following manner: a semitransparent Al film (100 Å) was first vacuum-deposited on a glass substrate, an organic thin film (2500–3000 Å) of the triad was then spin-coated from a chloroform solution, and finally, an Au-film covered electrode (100 Å) was vacuum-deposited. Under illumination from the Al side with a 24 mW/cm^2 tungsten–halogen lamp attached to a monochrometer, the generated photocurrents were measured and converted into the incident photon-to-current conversion efficiencies (IPCE). The photocurrents increased with the chain extension of the oligothiophene, similar to the case of the **nT–C$_{60}$** series. Figure 2 shows the action spectra of the **TTF–8T–C$_{60}$** and **TTF–12T–C$_{60}$** devices. When compared to the corresponding **nT–C$_{60}$** devices,[2a] the **TTF–nT–C$_{60}$** devices demonstrated somewhat higher photocurrents. On considering that TTF is poor as a light harvester, it is thus considered that the attached TTF in the triads contributes to the enhancement of photoinduced charge separation and/or charge migration, resulting in the increase of the photocurrent.

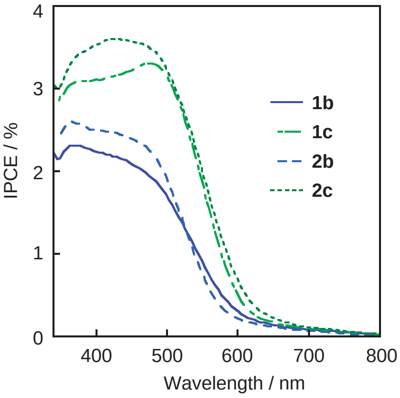


Figure 2. Photocurrent action spectra of the Al/**TTF–nT–C$_{60}$**/Au cells.

In conclusion, we have developed the **TTF–nT–C$_{60}$** triads as novel single-component photovoltaic materials. It has turned out that the additionally attached TTF contributes to some improvement of photovoltaic performances, when compared to the previous dyads **nT–C$_{60}$**.

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References and Notes

1 a) T. Otsubo, Y. Aso, K. Takimiya, *Pure Appl. Chem.* **2005**, *77*, 2003. b) J. L. Segura, N. Martín, D. M. Guldi, *Chem. Soc. Rev.* **2005**, *34*, 31.
2 a) N. Negishi, K. Yamada, K. Takimiya, Y. Aso, T. Otsubo, Y. Harima, *Chem. Lett.* **2003**, *32*, 404. b) N. Negishi, K. Takimiya, T. Otsubo, Y. Harima, Y. Aso, *Chem. Lett.* **2004**, *33*, 654. c) N. Negishi, K. Takimiya, T. Otsubo, Y. Harima, Y. Aso, *Synth. Met.* **2005**, *152*, 125.
3 a) T. Yamashiro, Y. Aso, T. Otsubo, H. Tang, Y. Harima, K. Yamashita, *Chem. Lett.* **1999**, 443. b) M. Fujitsuka, O. Ito, T. Yamashiro, Y. Aso, T. Otsubo, *J. Phys. Chem. A* **2000**, *104*, 4876. c) M. Fujitsuka, K. Matsumoto, O. Ito, T. Yamashiro, Y. Aso, T. Otsubo, *Res. Chem. Intermed.* **2001**, *27*, 73. d) M. Fujitsuka, A. Masuhara, H. Kasai, H. Oikawa, H. Nakanishi, O. Ito, T. Yamashiro, Y. Aso, T. Otsubo, *J. Phys. Chem. B* **2001**, *105*, 9930.
4 *TTF Chemistry*, ed. by J. Yamada, T. Sugimoto, Kodansha-Springer, Tokyo, **2004**.
5 H. Kanato, K. Takimiya, T. Otsubo, Y. Aso, T. Nakamura, Y. Araki, O. Ito, *J. Org. Chem.* **2004**, *69*, 7183.
6 M. Iyoda, Y. Kuwatani, N. Ueno, M. Oda, *J. Chem. Soc., Chem. Commun.* **1992**, 158.
7 M. Maggini, G. Scorrano, M. Prato, *J. Am. Chem. Soc.* **1993**, *115*, 9798.
8 All new compounds were satisfactorily characterized by spectroscopic measurements and elemental analyses.
9 Similar ferrocene–oligothiophene–fullerene triads showed efficient intramolecular electron transfer among the three chromophores. a) Ref. 5. b) T. Nakamura, H. Kanato, Y. Araki, O. Ito, K. Takimiya, T. Otsubo, Y. Aso, *J. Phys. Chem. A* **2006**, *110*, 3471.

Published on the web (Advance View) May 24, 2006; doi:10.1246/cl.2006.668