

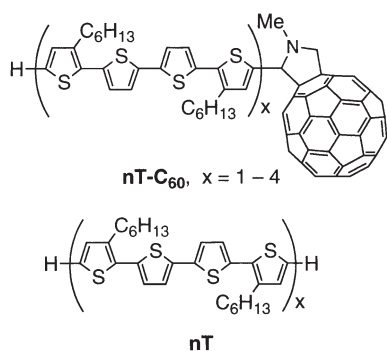
Oligothiophene/fullerene Dyads as Active Photovoltaic Materials

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Oligothiophene/fullerene dyads (**nT-C₆₀**) are incorporated in photovoltaic cells, which demonstrate relatively high incident photon-to-current efficiency. The monochromatic power conversion efficiency of the Al/**16T-C₆₀**/Au device measured at 456 nm is 0.4%.

Efficient photoinduced electron transfer from a conjugated polymer to a fullerene¹ has found application in low-cost plastic solar cells.² Early devices containing both components in a bilayer type gave only low performance for power conversion,³ but modified devices using a blend of both components in an active organic layer considerably improved solar power efficiency,⁴ which was recently enhanced up to 2.5%⁵ and 3.6%⁶ of the best class amongst solar cells of this type. Conjugated polymers modified with fullerenes have been recently studied in expectation of improved performance due to efficient intramolecular electron transfer from the polymer to the pendant fullerene.⁷ Some fullerene-bearing oligomers have also attracted much interest as single-component photovoltaic materials,⁸ but the efficiency of most of the devices made from them is limited by competition between the photoinduced electron transfer and energy transfer from the oligomer moiety to the fullerene. We recently discovered highly efficient photoinduced electron transfer for the oligothiophene/fullerene dyads **nT-C₆₀** in polar solvents⁹ and in solid state.¹⁰ The quantum yield for the charge separation process is nearly unity. This, as well as the intense absorption of oligothiophene chromophores in the visible region, has prompted us to investigate the potential of the dyads as photovoltaic materials. We here would like to report the remarkably high performance of the dyad-made photovoltaic cells, as compared not only to the cells using pristine oligothiophenes **nT** but also those previously reported for fullerene-bearing oligomers.



The sandwich device structure of Al/**nT-C₆₀**/Au was fabricated, as schematically depicted in Figure 1, where the organic layer was prepared by spin-coating from a chloroform solution on a vacuum-deposited semitransparent Al film.¹¹ The films of **nT-C₆₀** showed no fluorescence, suggesting effective quenching due

to electron transfer from the oligothiophene to the fullerene. Upon illumination from the Al side with $10 \mu\text{W cm}^{-2}$ monochromatic light, the photovoltaic cells showed marked photocurrents. The short-circuit currents (I_{sc}) are highly dependent on the oligothiophene chain lengths, and the visible parts of the action spectra are in strict accordance with the absorption spectra of the oligothiophene chromophores (Figure 2).

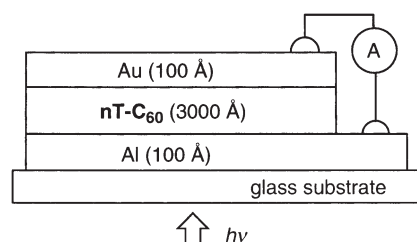


Figure 1. Schematic structure of the **nT-C₆₀**-based photovoltaic cell.

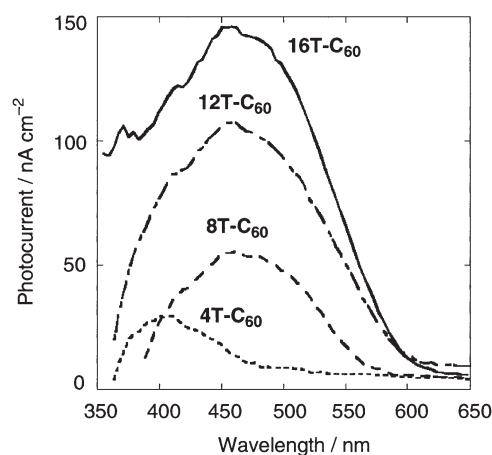


Figure 2. Photocurrent action spectra of the Al/**nT-C₆₀**/Au devices irradiated with $10 \mu\text{W cm}^{-2}$ light through the Al electrode.

Table 1 summarizes the incident photon-to-current efficiencies (IPCE) at maximum currents. The efficiencies of the photovoltaic cells using **nT-C₆₀** are larger by one order of magnitude than those of the cells using the pristine oligothiophenes **nT**. It is thus evident that the intramolecular electron transfer of the dyad system greatly contributes to the generation of photocurrent. The systematic increase of the photocurrent with the chain extension of the oligothiophene is in accordance with the observation that the electron transfer of the dyad containing a longer oligothiophene occurs more efficiently, because the lower oxidation potential of the long oligothiophene is more effective for lowering the energy level of the charge separated state.⁹

Alternative illumination from the Au side of the asymmetric

metal contact structure drastically decreased the photocurrents, and the action spectra were deformed to the longer wavelength side. This result, considering the higher work function of Au than that of Al, suggests that charge carriers are generated in the organic layer close to the Al electrode, and a good network of oligothiophenes for hole transport is set up.

Table 1. Performance characteristics of the photovoltaic devices

Comp.	$I_{sc}/\text{nA cm}^{-2}$	λ_{inc}/nm	IPCE/%
4T-C₆₀	30.4	410	2.1
8T-C₆₀	56.2	459	3.7
12T-C₆₀	108	461	7.0
16T-C₆₀	148	456	9.7
12T	5.1	460	0.3
16T	9.1	457	0.6

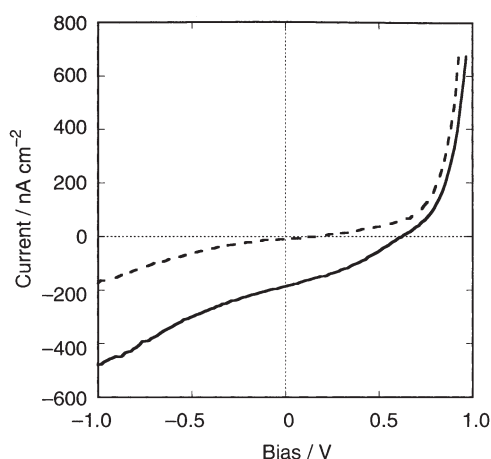


Figure 3. I-V characteristics of the Al/16T-C₆₀/Au device in the dark (broken line) and under 10 $\mu\text{W cm}^{-2}$ of illumination at 456 nm (solid line).

Figure 3 demonstrates the current-voltage characteristics of the most effective **16T-C₆₀** device in the dark and under illumination, which shows the open-circuit photovoltage of 0.64 V and the short-circuit current density of 190 nA cm^{-2} . The fill factor, a measure of the squareness of the I-V characteristics, is equal to 0.34. On the basis of these data, the monochromatic power conversion efficiency of the Al/16T-C₆₀/Au device is evaluated as 0.4%, which is reasonably high, as compared to those previously reported using oligomer/fullerene dyads.⁸

In summary, we have demonstrated that the oligothiophenes/fullerene dyads are efficient single-component materials for photovoltaic cells. The generation of high photocurrents is ascribable to the ready photoinduced charge separation of the dyads and a good oligothiophene network for hole transport.

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This paper is dedicated to Emeritus Professor Soichi Misumi on the occasion of his 77th birthday.

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- The syntheses of the three oligothiophene/fullerene dyads **4T-C₆₀**, **8T-C₆₀** and **12T-C₆₀** were reported in the previous paper: T. Yamashiro, Y. Aso, T. Otsubo, H. Tang, Y. Harima, and K. Yamashita, *Chem. Lett.*, **1999**, 443. The new compound **16T-C₆₀** was prepared by the same method.