Development and Photovoltaic Performance of Oligothiophene-sensitized TiO_2 Solar Cells

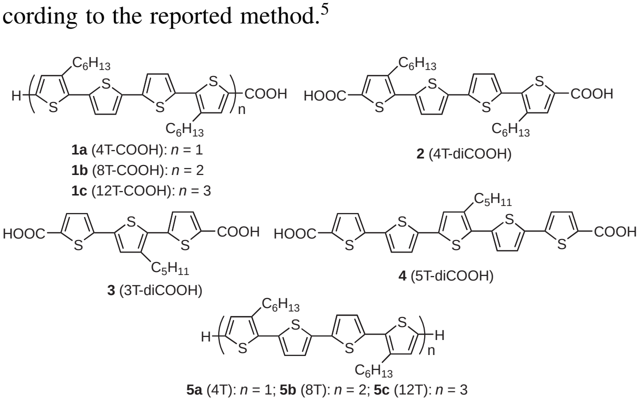
Koki Tanaka, Kazuo Takimiya, Tetsuo Otsubo,* Koji Kawabuchi, Shotaro Kajihara, and Yutaka Harima*
Department of Applied Chemistry, Graduate School of Engineering, Hiroshima University,
Higashi-Hiroshima 739-8527

(Received March 6, 2006; CL-060267; E-mail: otsubo@hiroshima-u.ac.jp)

Novel dye-sensitized TiO_2 solar cells have been developed using a variety of oligothiophenecarboxylic acids. These cells showed relatively high photovoltaic performances ($\eta = 0.41$–1.29%), which are largely dependent on the chain lengths of the oligothiophenes and the number of the carboxylic groups.

Oligothiophenes are promising candidates for advanced molecular electronics materials owing to high photo- and redox-activities, high charge-transport abilities, and high environmental stabilities.[1] We recently found that fullerene-linked oligothiophenes are very useful as active one-component materials in plastic photovoltaic devices.[2] The strong absorptions of oligothiophene chromophores to visible light have led us to expect that they are also applicable to currently attractive dye-sensitized solar cells.[3] To make sure of this, we have intended to examine the solar cells of nanocrystalline TiO_2 electrodes adsorbing monocarboxylic acids (**1a**–**1c**, *n*T-COOH) with different chain lengths and quaterthiophenedicarboxylic acid (**2**, 4T-diCOOH). In this connection, Yanagida and co-workers recently reported the efficient polythiophene-sensitized metal oxide photovoltaic cells.[4] In addition, during our research, Zhu and co-workers reported high photovoltaic performances of dye-sensitized solar cells using terthiophenedicarboxylic acid (**3**, 3T-diCOOH) and quinquethiophenedicarboxylic acid (**4**, 5T-diCOOH).[5] Here, we like to report the photovoltaic performances of **1a**–**1c** and **2** in comparison to those of **3** and **4** (Scheme 1).

The oligothiophene monocarboxylic acids **1a**–**1c** were prepared in reasonable yields by treatments of the corresponding oligothiophenes (**5a**–**5c**)[6] with 1.1 equivalent butyllithium in dry THF at rt, followed by quenching with excess dry ice: **1a**, 53% yield; **1b**, 42% yield; **1c**, 38% yield.[7] The quaterthiophene dicarboxylic acid **2** was also prepared in 60% yield from quaterthiophene **5a** by a similar treatment except use of two equivalent butyllithium. For comparison, the terthiophenedicarboxylic acid **3** and quinquethiophenedicarboxylic acid **4** were prepared according to the reported method.[5]



Scheme 1.

The TiO_2 electrodes used for dye-sensitized solar cells were prepared as follows. Into a powder (1.30 g) of TiO_2 (Japan Aerosil, P25, $d = 30$–40 nm) in a mortar was added water (1.9 mL) in six portions with well stirring. Then, three drops of 12 M nitric acid and polyethylene glycol (80 mg) were successively added, and the mixture was well kneaded to a smooth paste. It was then applied on a fluorine-doped tin-oxide (FTO) substrate and sintered for 30 min at 500 °C. Thus, the obtained 6–7-μm thick TiO_2 substrate was cut to a $0.5 \times 0.5\,\mathrm{cm}^2$ square and immersed into a 0.3 mM DMF solution of the oligothiophenecarboxylic acid for 3 h enough to adsorb the photosensitizer. The amount of the dye adsorbed on nanocrystalline TiO_2 was estimated by spectroscopically analyzing the amount of the dye desorbed by treatment with a 6:3:1 v/v mixed solution of THF–DMF–(1 M aq NaOH). It turned out that the oligothiophene monocarboxylic acids **1a**–**1c** were adsorbed on nanocrystalline TiO_2 within 3 h, and the adsorbed amounts were independent of the oligothiophene chain lengths: **1a**, $0.88 \times 10^{-7}\,\mathrm{mol\,cm^{-2}}$; **1b**, $0.87 \times 10^{-7}\,\mathrm{mol\,cm^{-2}}$; **1c**, $0.87 \times 10^{-7}\,\mathrm{mol\,cm^{-2}}$. The quaterthiophenedicarboxylic acid **2** was adsorbed in a somewhat larger amount ($1.03 \times 10^{-7}\,\mathrm{mol\,cm^{-2}}$). Evidently, two COOH groups promote the dye adsorption more efficiently than one COOH group.

The dye-sensitized solar cells were fabricated by using the thus obtained TiO_2 working electrodes, platinum-coated glass as a counter electrode, and a solution of 0.05 M iodine and 0.5 M lithium iodide in acetonitrile as electrolyte. The photocurrents of oligothiophene-sensitized solar cells were measured under monochromatic irradiation with a Shimadzu AT-100 HG halogen lamp. Figure 1 shows the wavelength-dependent spectra of the incident photon-to-current conversion efficiency (IPCE) of the **1a**–**1c** and **2**-based solar cells in the visible region. The action spectra are considerably broadened and roughly similar to

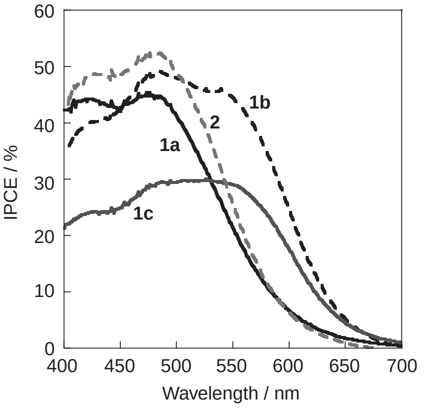


Figure 1. IPCE spectra of dye-sensitized solar cells based on oligothiophenecarboxylic acids **1a**–**1c** and **2**.

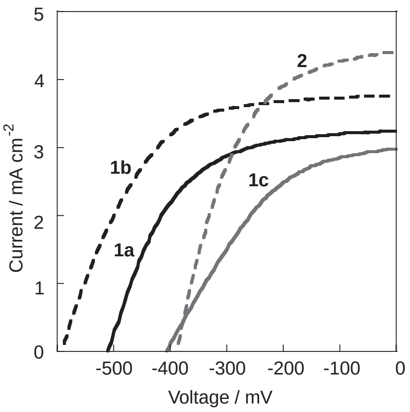


Figure 2. Current–voltage curves of dye-sensitized solar cells based on oligothiophenecarboxylic acids **1a**–**1c** and **2**.

the electronic absorption bands of the respective oligothiophenecarboxylic acids in the solid phase: **1a**, $\lambda_{\max}$ 436 nm; **1b**, $\lambda_{\max}$ 485 nm; **1c**, $\lambda_{\max}$ 510 nm; **2**, $\lambda_{\max}$ 460 nm. The IPCE of the 4T-COOH coated cell in the short wavelength region is reasonably high with maximum 45% at 476 nm. Thanks to the more extensive conjugation of octithiophene chromophore, the action spectrum of the 8T-COOH coated cell extends to the longer wavelength region, and the maximum IPCE is 49% at 490 nm. Evidently, the more effective absorption of 8T-COOH to longer wavelength visible light is responsible for the enhancement of IPCE. In contrast, the photocurrent of the 12T-COOH coated cell markedly decreases, though the absorption of the dodecithiophene similarly extends to longer wavelength region. The 4T-diCOOH coated cell demonstrates somewhat higher IPCE over a whole visible range than that of the 4T-COOH coated cell, reflecting the above-indicated increasing amount of the dicarboxylated dye.

Figure 2 shows photocurrent–voltage characteristics of the **1a**–**1c**-based cells under the AM 1.5 simulated solar irradiation of 100 mW cm^{-2} Xe lamp. The short-circuit current densities (I_{SC}), open-circuit voltages (V_{OC}), fill factors (*ff*), and power conversion efficiencies (η) together with those of the photovoltaic cells using the oligothiophenedicarboxylic acids **2**–**4** are summarized in Table 1.

Consistent with the above IPCE data, the power conversion efficiencies of oligothiophenecarboxylic acid cells follow in the order of 8T-COOH (1.29%), 4T-COOH (0.92%), and 12T-COOH (0.55%). The higher performance of 8T-COOH than that of 4T-COOH can be explained by ready electron migration from excited octithiophene to TiO_2 due to the enhanced charge stabilizing ability of longer oligothiophene.[8] On the other hand, the low performance of 12T-COOH is ascribable to its too high HOMO level. Cyclic voltammograms indicated a marked lowering of the first half-wave potentials with the chain extension of oligothiophenes: **1a**, E_{pa} 0.95 V; **1b**, E_{pa} 0.68 V; **1c**, E_{pa} 0.45 V.[9] Thus, it is considered that the approach of the half-wave potential of **1c** to the redox potential (0.2 V) of I^-/I_3^- leads to difficult electron supply from the latter electrolyte.[10]

Although the 4T-diCOOH coated cell showed higher IPCE than the 4T-COOH cell, it is unexpected that the power conversion efficiencies of both cells are nearly the same. It should be noticed that the higher short-circuit current density (I_{SC}) is compensated by the lower open-circuit voltage (V_{OC}). In addition, the less effective power conversion efficiencies of solar cells using **3** and **4** are ascribable partly to the low open-circuit voltages. It is speculated that the dicarboxylated groups force molecular arrangements close to the TiO_2 electrode, resulting in the lowering of photovoltages due to enhanced quenching process.[11]

Table 1. Photovoltaic performances of oligothiophene-sensitized solar cells[a]

Comp.	I_{SC}/mA cm^{-2}	V_{OC}/mV	*ff*	η/%
1a	3.38	496	0.55	0.92
1b	3.74	596	0.58	1.29
1c	2.98	408	0.45	0.55
2	4.33	392	0.52	0.89
3	1.99	384	0.54	0.41
4	3.77	436	0.50	0.82

In conclusion, we have developed novel dye-sensitized TiO_2 solar cells using a variety of oligothiophenecarboxylic acids. The present systematic research has provided useful information on the potential of oligothiophene materials for dye-sensitized solar cells.

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

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Published on the web (Advance View) April 29, 2006; doi:10.1246/cl.2006.592