

# ETM011 Highly Efficient Organic-Inorganic Bulk-Heterojunction Solar Cells Based on Metal Alkoxide

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#### Abstract

The number of publications concerned with typical bulk-heterojunction solar cells that use fullerene derivatives or n-type semiconducting polymers as electron acceptors has grown very rapidly. In this work, we present novel Ti-alkoxides as electron acceptors in the photoactive layers of bulk-heterojunction solar cells. We obtained high performance when we used titanium(IV) ethoxide or isopropoxide as an electron acceptor. With these Ti(IV) alkoxides, the electron donors and acceptors formed suitable phase-separated structures for charge separation and charge transfer in the photoactive layer. We fabricated all-printed bulk-heterojunction solar cells using Ti-alkoxides as the electron acceptors, and observed energy conversion efficiencies that nearly reached the values obtained with the fullerene systems.

*Keywords*: Energy conversion, Solar cells, Thin film solar cells, Photovoltaic cells, Morphology control, Bulk heterojunction solar cells

#### **1. Introduction**

Organic photovoltaic devices constitute a rapidly emerging technological area because of their promising properties, including flexibility, light weight, transparency, low cost, and large-area manufacturing compatibility[1-3]. In recent years, dye-sensitized solar cells and organic thin-film solar cells have been reported as next-generation developments in this area. Above all, as organic thin-film solar cells, bulkheterojunction organic thin-film solar cells using organic semiconducting polymers have been one of the most extensively studied research subjects. Commonly, the photoactive layers of these devices are composed of p-type semiconducting polymers and n-type fullerene derivatives such as [6,6]-phenyl-C61 or C71butyric acid methyl ester ([60]PCBM or [70]PCBM) [4, 5]. On the other hand, several reports have described new types of organic thin-film solar cells that use conjugated polymers as n-type semiconductors [6, 7]. Furthermore, a previous study reported the formation of fullerene-free organic-inorganic thin-film solar cells utilizing Ti(IV) isopropoxide as the electron acceptor [8]. These reports have inspired the development of fullerene-free organic thin-film solar cells. Because the band gap of the electron acceptor can be adjusted easily, high photoconversion efficiencies can be expected. However, the discussion pertaining to the ability of the morphology of the photo-active layer to function in terms of charge separation and charge transfer is insufficient compared with that of the fullerene system or n-type semiconducting polymer systems, because these

systems are soluble in many solvents, which facilitates the control of their morphology by changing the solvent of the ink. In the case of these systems, many studies have shown that morphology control is an important method for increasing the performance [9]. In contrast, in the case of an inorganic electron acceptor used in combination with a polymer as the electron donor, there are few solvents capable of dissolving both semiconductors. Here, we present an organic-inorganic hybrid bulk-heterojunction thin-film solar cell that uses a polymer and Ti-alkoxides for next-generation fullerene-free thin-film solar cells. In particular, this research focused on the molecular structure of the Ti-alkoxide used as the electron acceptor, as well as its influence on the control of the phase separation in the photoactive layer, in order to obtain highly efficient organic-inorganic thin-film solar cells.

#### 2. Experimental

#### 2.1 Materials

We purchased poly[2,7-(9,9-dioctylfluorene)-alt-4,7bis(thiophen-2-yl)benzo-2,1,3-thiadiazole] (PFO-DBT, electron donor) as a p-type semiconducting polymer from Sigma–Aldrich. The n-type semiconductors— Ti(IV) isopropoxide, Ti(IV) ethoxide, Ti(IV) butoxide, and a Ti(IV) butoxide polymer—were also purchased from Sigma-Aldrich, as was the commonly available [60]PCBM, which was used as a reference. The molecular structures of these materials are shown in Fig. 1.

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Fig. 1 Chemical structures of PFO-DBT and Ti-alkoxides

#### 2.2 Solar cells fabrication

Indium-tin oxide (ITO)-coated glass substrates (15  $\Omega$  per square) were patterned to fabricate the solar cells. These substrates were successively washed by ultrasonication in water, acetone, and isopropyl alcohol for 15 min each, and then dried in a stream of dry air. The washed substrates were further treated with a UV-O<sub>3</sub> cleaner (Filgen, Model UV253E) for 20 min. A photoactive layer of PFO-DBT/[60]PCBM or PFO-DBT/Ti-alkoxide (1:2 wt%) was spin-coated on the ITO substrates at 2000 to 3500 rpm for 20 s from chlorobenzene solution. All photoactive layers were dried under dark conditions. The photoactive layers were about 60 nm thick. An organic electrode (50 nm) was coated by screen printer (Mitani Micronics, Model MEC-2400). purchased poly(3,4-We ethylenedioxythiophene)-poly(styrenesulfonate)

(PEDOT-PSS, Clevios S V3) from Baytron to form the organic electrodes. The photoactive layer and organic electrodes were laminated with an epoxy resin. Figure 2 shows the device structure.



Fig. 2 Device structure of all-printed bulk heterojunction solar cells

#### 2.3 Measurement

The current density-voltage (J-V) characteristics were measured using a direct-current voltage and a current source/monitor under illumination with AM1.5G simulated solar light (San-Ei Electric, XES-40S1) at 100 mW/cm<sup>2</sup>. The incident photon-to-current efficiency (IPCE) of the devices was measured with a direct-current voltage and a current source/monitor (Bunko-Keiki Co., CEP-2000RS) under illumination with AM1.5G simulated solar light at 100 mW/cm<sup>2</sup>. The light intensity was corrected against a calibrated silicon photodiode reference cell (Bunko-Keiki, BS-520). The phase separation structures of the photoactive layers were investigated by scanning electron microscopy (SEM, JEOL Ltd., JSM-7800).



#### 3. Results and Discussion

The energy level and band gap of PFO-DBT and each Ti-alkoxide are shown in Table 1, as calculated using the ionic potential values and the optical absorption spectra. Based on these data, the energy levels of the Ti-alkoxides and PFO-DBT are considered sufficient to effect charge separation for carrier generation at p/n surfaces.

Table. 1 Energy levels and band gaps of PFO-DBT and the Ti-alkoxides

	PFO-DBT	Titanium(IV)	Titanium(IV)	Titanium(IV)	Titanium(IV)
		isopropoxide	ethoxide	butoxide	butoxide polymer
HOMO	5.4	7.49	7.55	7.53	7.57
Level [eV]					
LUMO	3.53	3.86	3.90	3.76	3.83
Level [eV]					
Energy Gap [eV]	1.87	3.63	3.65	3.77	3.74

Next, we fabricated bulk-heterojunction solar cells and investigated their photovoltaic performance [9, 10]. The J-V characteristics of the bulk-heterojunction solar cell for each Ti-alkoxide are shown in Figure 3.



Fig. 3 J-V curves of bulk-heterojunction solar cells based on the Ti-alkoxides and PFO-DBT

When the Ti(IV) isoproposide, ethoside, or butoxide was mixed with PFO-DBT, photocurrent generation was clearly observed. The Ti(IV) isoproposide and ethoxide devices exhibited higher Jsc values than the Ti(IV) butoxide device. The Ti(IV) butoxide polymer device exhibited the lowest Jsc value, 25  $uA/cm^2$ . To verify these results, we investigated the phase separation in the photoactive layer. A phase-separated structure in the photoactive layer of a bulkheterojunction solar cell is an important factor in the overall photovoltaic performance [11]. We considered three typical phase-separation models for evaluating charge separation and charge transfer in the photoactive layer. We also examined the Jsc values of the devices, which are associated with these phaseseparation models. That is, we evaluated the phaseseparation model in association with the Jsc value for the devices, when considering charge separation and

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charge transfer in the photoactive layer. The relationships between the phase-separation models and the Jsc values of the devices are shown in Table 2.

Table. 2 Phase-separation models of the photoactive layers in bulk-heterojunction solar cells

Phase Separation Model	(A)	(B)	
Phase Separation	coarse	medium	fine
Continuity	continuous	continuous	isolated
Current Density	low	high	low

In Model A (Table 2), when the phase areas of both semiconducting materials which form the photoactive layer are too large, the production of a sufficient number of p/n junction surfaces for charge separation would be inhibited. In contrast, in Model C, the respective phases are formed in isolation, which would inhibit the charge transfer of free carriers to both electrodes. Ideally, the phase structure that is required would be continuous and moderately fine, such as indicated by Model B in Table 2. In consideration of this analysis, the morphologies of the photoactive layers were investigated by SEM [11, 12], and the resulting images are shown in Table 3.

Table. 3 SEM images of photoactive layers based on Ti-alkoxides.



When the Ti(IV) butoxide polymer was mixed with PFO-DBT, a phase-separated structure was formed with large phase domains. Consequently, this photoactive layer morphology was unsuitable for the generation of charge separation for a high Jsc. In the case of Ti(IV) butoxide, the constructed morphology consisted of isolated and extremely compact domains. This morphology also fails to deliver higher Jsc values, because the isolated phase domains hinder charge transfer of the free carriers to both electrodes. On the other hand, when Ti(IV) isopropoxide or ethoxide was mixed with PFO-DBT, the resulting morphologies were moderately fine and had adequate continuity. In other words, enough p/n junction interfaces were formed for charge separation, and the free carriers reached both electrodes smoothly.

We can account for these phenomena primarily as follows. When the Ti-butoxide polymer is used, it selforganizes preferentially, resulting in the coarsening of the formed phase. In the case of Ti(IV) butoxide as the electron acceptor, the self-organization of the conjugated polymer as the electron donor is hindered by the bulky chemical Ti(IV) butoxide structure: this material is bulkier than the other Ti-alkoxide monomers as n-type semiconductors. Thus, Ti(IV) isopropoxide and ethoxide were suitable as electron acceptors with respect to phase separation for this PFO-DBT system. Finally, we fabricated a fullerene-[60]PCBM/conjugated based polymer bulkheterojunction solar cell for comparison with the Ti(IV) isopropoxide/conjugated polymer system. The comparative J-V curves and IPCE spectra and Performance parameters are shown in Figures 4 and 5, Table 4.



Fig. 4 J-V curves of all-printed bulk-heterojunction solar cells based on Ti(IV) isopropoxide and [60]PCBM



Fig. 5 IPCE spectra of all-printed bulk-heterojunction solar cells based on Ti(IV) isopropoxide and [60]PCBM.

In both cases, the bulk-heterojunction all-printed solar cells using organic electrodes afforded nearly the same Jsc.



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Table. 4 Performance parameters of solar cells.

	Titanium(IV) isopropoxide/PFO-DBT	[60]PCBM/PFO-DBT
Jsc [µA/cm <sup>2</sup> ]	191	195
Voc [V]	0.53	0.6
Fill factor	0.31	0.31
Efficiency [%]	0.031	0.036

### 4. Conclusion

This work demonstrates that a novel organicinorganic photoactive layer consisting of а semiconducting polymer as the electron donor and a Ti-alkoxide as the electron acceptor can function in a bulk-heterojunction solar cell. We found that the control of phase separation was important for highly efficient bulk-heterojunction solar cells, not only for fullerene systems but also for Ti-alkoxide systems. The systems employing Ti(IV) isoproposide and Ti(IV) ethoxide as the electron acceptors generated higher Jsc than the other Ti-alkoxide materials. Thus, the photoactive layers fabricated with Ti( IV ) isopropoxide and Ti(IV) ethoxide achieved structural phase separations that were suitable for both charge separation and charge transfer. For the future development of organic-inorganic bulk-heterojunction solar cells, controlling the hydrolysis of the Tialkoxide to improve charge transfer ability and fabricating a buffer layer at the electrodes for charge collection are necessary to realize higher energy conversion efficiencies and performance.

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