# Fundamental Study on Organic Solar Cells based on Soluble ZnPc

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### 1. Introduction

The materials to be often used for organic thin film solar cells are  $\pi$ -conjugated polymer, fullerene derivative, porphyrin and phthalocyanine. Phthalocyanine is well known as stable dye which has strong absorption at long wavelength region (600-800 nm), and it is used as donor material for organic solar cells with fullerene as acceptor material [1,2]. However these solar cells were fabricated by vacuum deposition because of poor solubility or insolubility of phthalocyanine in almost every solvent [1-4]. The advantages of the organic thin film solar cells over the inorganic solar are low cost and easy processing due to "solution based processes". Therefore, a high solubility in solvents is an important factor for organic solar cell materials.

The solubility of phthalocyanine can be improved by adding proper substituent on the ring of phthalocyanine. Various dissoluble phthalocyanine derivatives have been synthesized [5,6], and organic devices based on some of these phthalocyanine were reported [7,8]. Our synthesized zinc phthalocyanine ((TFEO<sub>4</sub>)<sub>4</sub>-ZnPc) is shown in Fig 1, which also exhibits high solubility in some organic solvent due to trifluoroethoxy (TFEO) substituent. On the other hand, it is well known that substituents on the ring of phthalocyanine [5,9]. Due to electron-withdrawing property of substituent including fluorine, (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc may act as acceptor material. This is opposite property of previous dissoluble phthalocyanine derivatives, which are donor material [7,8].

In this study, we investigated the property of  $(TFEO_4)_4$ -ZnPc as a material for organic thin film solar cell, and fabricated solar cells based on  $(TFEO_4)_4$ -ZnPc.

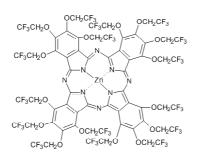


Fig 1. Structures of trifluoroethoxy coated zinc phthalocyanine ((TFEO<sub>4</sub>)<sub>4</sub>-ZnPc)

#### 2. Result and Discussion

#### Electrochemical Characterization

The electrochemical oxidation potentials of  $(TFEO_4)_4$ -ZnPc and tetra-tert-butyl zinc phthalocyanine (tBu<sub>4</sub>-ZnPc), as a reference, were investigated by the cyclic voltammetry in acetonitrile with 0.1M TBAPF<sub>6</sub>. The cyclic voltammogram of (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc is shown in Fig. 2. The HOMO energy levels of each ZnPc can be determined from the first oxidation potentials [10]. On the other hand, the LUMO energy levels can be approximated from HOMO energy level and energy band gap  $(E_g)$  obtained from UV/vis absorption spectra. HOMO and LUMO energy level and E<sub>g</sub> are summarized in Table I. LUMO energy level of (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc is lower than tBu<sub>4</sub>-ZnPc, which is approximate to LUMO energy level of PCBM as acceptor material, not P3HT as donor material. These result indicate TFEO-substituent decrease energy level of ZnPc, and  $(TFEO_4)_4$ -ZnPc can be used as an acceptor material.

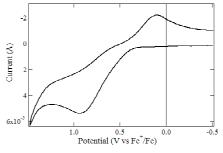


Fig 2. The cyclic voltammogram of  $(TFEO_4)_4$ -ZnPc (vs Fe<sup>+</sup>/Fe)

Table I Energy levels of the HOMO/LUMO and Energy band gap for (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc, *t*Bu<sub>4</sub>-ZnPc, PCBM and P3HT

Compound	HOMO (eV)	LUMO (eV)	E <sub>g</sub> (eV)
(TFEO <sub>4</sub> ) <sub>4</sub> -ZnPc	-5.66	-3.98	1.68
<i>t</i> Bu <sub>4</sub> -ZnPc	-5.27	-3.50	1.77
PCBM	-6.1	-4.2	-
РЗНТ	-5.1	-3.2	-

Solar Cell Characterization

We fabricated two type organic thin film solar cells with  $(TFEO_4)_4$ -ZnPc, one is based on only  $(TFEO_4)_4$ -ZnPc,

another is based on P3HT as donor material and  $(TFEO_4)_4$ -ZnPc as acceptor material (heterojunction solar cell). The solar cell based on only P3HT was also fabricated, as reference. For each solar cell, Poly (3,4-ethylenedioxythiophe ne)/poly (styrenesulfonate) (PEDOT/PSS), as anode buffer layer, was spin-coated on an indium tin oxide (ITO) coated glass substrate and annealed. For single layer solar cell, (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc as photo active layer was spin-coated on PEDOT/PSS layer from acetone, and annealed. On the other hand, for heterojunction solar cell, P3HT as donor spin-coated layer was on PEDOT/PSS from o-dichlorobenzene, then (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc as acceptor layer was spin-coated from acetone. P3HT is insoluble in acetone, thus P3HT layer is not damaged by spin-casting of (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc, and annealed at 140 or 200 °C. The solar cell with only P3HT was also spin-coated from ODCB. The top electrode of Al was deposited by a vacuum deposition on the active layer for both solar cells. The properties of the solar cells were measured by using solar simulator (100 mW/cm<sup>2</sup>, AM 1.5 illumination) in air.

The photovoltaic parameters,  $J_{sc}$  (short circuit current density),  $V_{oc}$  (open circuit voltage), FF (fill factor), and  $E_{ff}$  (solar cell conversion efficiency) of each solar cell are summarized in Table II, and spectral responsivity for each solar cells annealed at 200 °C are shown in Fig.3.

Table IIThe characteristics of solar cells

Solar Cell	$E_{\rm ff}(\%)$	FF	$V_{oc}(V)$	J <sub>sc</sub> (mA/cm <sup>2</sup> )
(TFEO <sub>4</sub> ) <sub>4</sub> -ZnPc (140 °C)	2.0x10 <sup>-6</sup>	0.15	0.01	1.4x10 <sup>-3</sup>
(TFEO <sub>4</sub> ) <sub>4</sub> -ZnPc (200 °C)	1.6x10 <sup>-5</sup>	0.24	0.10	7.2x10 <sup>-4</sup>
Heterojunction (140 °C)	4.6x10 <sup>-3</sup>	0.27	0.29	5.9x10 <sup>-2</sup>
Heterojunction (200 °C)	3.3x10 <sup>-2</sup>	0.29	0.24	4.8x10 <sup>-1</sup>
P3HT (140 °C)	3.4x10 <sup>-3</sup>	0.31	0.57	1.9x10 <sup>-2</sup>
P3HT (200 °C)	2.9x10 <sup>-3</sup>	0.32	0.38	2.4x10 <sup>-2</sup>

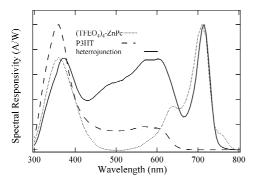


Fig. 3. Spectral responsivity for the solar cell based on  $(TFEO_4)_4$ -ZnPc, P3HT and Heterojunction solar cell

The solar cell based on only (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc performed photoelectric transfer, however, the values of solar cell efficiency were very low even though E<sub>ff</sub> was improved due to increase annealing temperature. On the other hand, the heterojunction solar cells were increased their solar cell efficiencies compared with the solar cell based on only P3HT. Fig. 3 shows that the spectral responsivity for the heterojunction solar cell has both wavelength region for (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc and P3HT. The heterojunction solar cell was increased E<sub>ff</sub> from  $4.6 \times 10^{-3}$  % to  $3.3 \times 10^{-2}$  % by raising anneal temperature from 140 °C to 200 °C, which is considered due to (TFEO<sub>4</sub>)<sub>4</sub>-ZnPc layer property was changed by high temperature near 200 °C.

# 3. Conclusions

In this study, the dissoluble ZnPc,  $(TFEO_4)_4$ -ZnPc was proved to be able to use as acceptor material for organic thin film solar cell by CV and solar cell measurement. The solar cell based on only  $(TFEO_4)_4$ -ZnPc showed low solar efficiency, however, the heterojunction solar cell with  $(TFEO_4)_4$ -ZnPc and P3HT showed higher solar cell efficiency than only  $(TFEO_4)_4$ -ZnPc and P3HT.

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