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Enhanced Performance of Organic Photovoltaic Cells Using F_4-TCNQ-PEDOT:PSS Films as a Hole Conducting Layer

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In this study, tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ)-doped poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) was spin-coated on a pre-patterned ITO glass and used as hole conducting layer materials in organic photovoltaic cells. The multi-layered ITO/F_4-TCNQ-PEDOT:PSS/CuPc/CuPc:C60/C60/BCP/Al organic photovoltaic cells were fabricated to evaluate the $J-V$ characteristics such as short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and energy conversion efficiency (η_e) of the device. A higher power conversion efficiency obtained from the device with a concentration of 0.1 wt% F_4-TCNQ in the PEDOT:PSS layer was achieved compared to those adopted from device without F_4-TCNQ doping in the PEDOT:PSS layer, and current density-voltage characteristics was also improved well with incorporation of F_4-TCNQ in PEDOT:PSS films.

Keywords CuPc/C60; F_4-TCNQ; organic photovoltaic cell; PEDOT:PSS; power conversion efficiency

Introduction

Organic photovoltaic cells have one of most attractive topics in the field of current renewable energy research because of their unique properties such as low cost of fabrication, light weight and easy processing [1,2]. In last decade, the performance of organic photovoltaic cells has been steadily improved and recently has exceeded 6% [3,4]. Many efforts have been made to enhance the efficiency of organic photovoltaic cells because the power conversion efficiency of organic photovoltaic cells is still low compared to their inorganic counterparts. Research activities have been focused on i) improving the work function of the electrode with different surface treatments [5,6], ii) incorporating another organic dopants into hole or electron transporting layer [7,8], iii) and inserting a buffer layer between the electrode and hole or electron transporting layer [9]. Among these efforts, the p-doping of hole transport layer has

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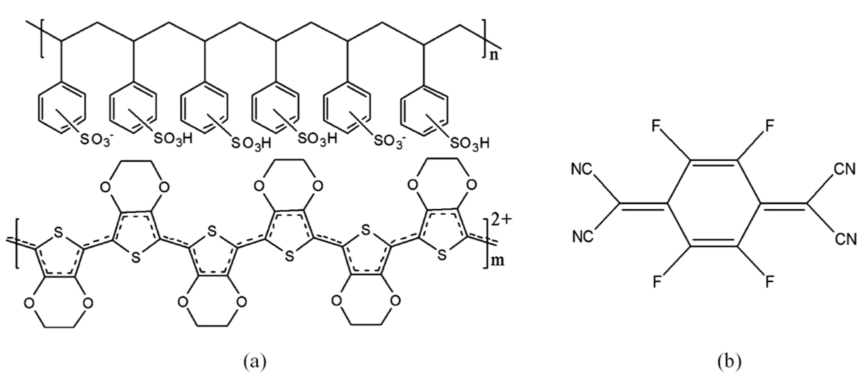
drawn many attentions because of its ability to enhance hole injection and lower turn-on voltage especially in organic light-emitting devices (OLEDs). As a dopant as well as a strong electron acceptor in a hole transport layer, tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) can be used to achieve efficient carrier injection by tunneling effect in a hole transport layer in organic photovoltaic cells and OLEDS. The dopant F_4-TCNQ increases its acceptor effect as already known from other classes of molecules [10–12]. Doping F_4-TCNQ in the organic photovoltaic cell is expected to balance the carrier mobility of the acceptor and donor and thus improve the carrier collection efficiency. Moreover, Conducting polymers, such as poly (3,4-ethylenedioxythiophene):poly (styrene sulfonate) (PEDOT:PSS) were often used as hole conducting layer materials for organic photovoltaic cells, since its ionization potential is close to the work function of ITO and its electron affinity, which is about 2.2 eV, is low enough to block electrons [13]. Recently, the conductivity modification of PEDOT:PSS has been attempted by adding inorganic, metals, small molecular organics and various solvents [14–16]. The incorporation of these materials into devices was revealed excellent electrical properties with better performance because these additives possess high conductivity and high work functions [17,18].

In this work, F_4-TCNQ doped PEDOT:PSS films were prepared and used as a hole conducting layer for organic photovoltaic device. The multi-layered ITO/F_4-TCNQ-PEDOT:PSS/CuPc/CuPc(1):C60(1)/C60/BCP/Al devices were fabricated and the current density-voltage characteristics and power conversion efficiency were investigated. Different doping amount of F_4-TCNQ were embedded in PEDOT:PSS. Because of the high electron affinity of F_4-TCNQ, it is expected that the hole collecting and hole conducting ability of PEDOT:PSS might be improved in organic photovoltaic cells.

Experimental

ITO/F_4-TCNQ-PEDOT:PSS [35 nm]/CuPc [15 nm]/CuPc(1):C60(1) [10 nm]/C60 [35 nm]/BCP [10 nm]/Al [100 nm] organic photovoltaic cells were fabricated to investigate the effect of F_4-TCNQ doping on the device performance. PEDOT:PSS poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (Baytron P from H. C. Starck GmbH) as a hole injection layer material was spin-coated on to the pre-patterned ITO glass substrate (15 Ω/sq). Copper phthalocyanine (CuPc,



(a) (b)

Figure 1. Chemical structure of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) (a), Tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) (b).

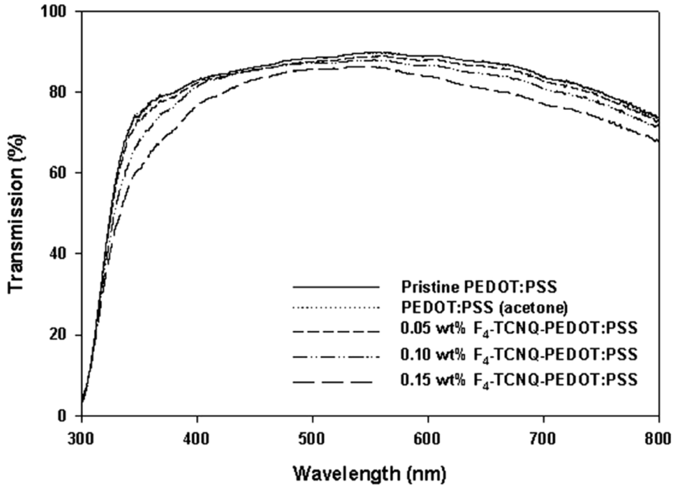


Figure 2. Transmission spectra of the F_4-TCNQ-PEDOT:PSS films.

formula: $C_{32}H_{16}CuN_8$, molecular weight: 576.078, melting point: >360°C, T_g: 240°C, Tokyo Kasei Kogyo Co. Ltd.) as a hole transport layer was sublimed to obtain thin films via vacuum process. Tetrafluoro-tetracyano-quinodimethane (F_4-TCNQ) as a dopant (formula: $C_{44}H_{32}N_2$, molecular weight: 276.15, melting point: >285°C, Sigma Aldrich, 97%) and C60 (Fullerene) as a electron transport layer (formula: C_{60}, molecular weight: 720.64, melting point: >280°C, T_g: 174°C, Sigma Aldrich, 99.5%) were used. As an electron blocking layer (EBL) material, bathocuproine (BCP, Acros Organics) was used in the device. The chemical structures of PEDOT:PSS and F_4-TCNQ are shown in Figure 1.

A 5% solution of PEDOT:PSS with F_4-TCNQ dopant (co-solvent:acetone) was spin-coated on to the pre-cleaned ITO glass substrate at a rotational speed of 2000 rpm for 15 s, then baked to dry F_4-TCNQ doped PEDOT:PSS film for 1 h at

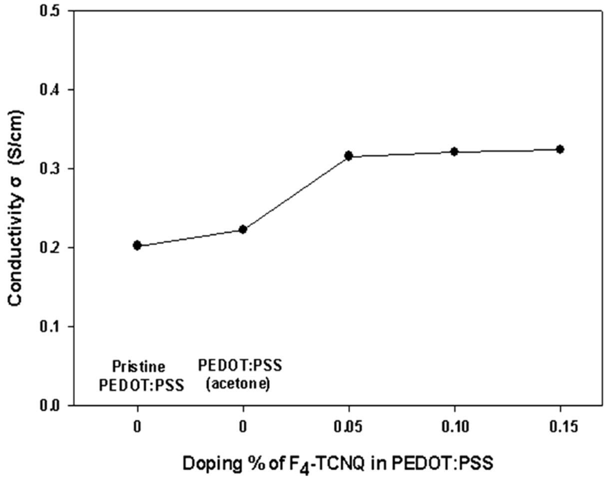


Figure 3. Conductivity of the F_4-TCNQ-PEDOT:PSS films.

90°C in a vacuum oven. In the current photovoltaic cells, the doping percent of F_4-TCNQ was 0.05, 0.1, and 0.15 wt%. CuPc and CuPc:C60 (blending ratio = 1:1) were deposited onto the PEDOT:PSS layer and the deposition rate was controlled to about 1.1 Å/s. CuPc:C60 film was obtained by co-evaporation. Thickness of each layer was measured using well calibrated quartz crystal thickness monitor (CRTM-6000, ULVAC kiko. Ltd.). An active area of device was made using a shadow mask to be 2 mm × 2 mm in dimension. The current density-voltage (J-V) and power conversion efficiency (η_e) characteristics were measured and calculated using Keithley 2400 multi-source meter unit. The Xenon lamp (100 mW/cm^2) was used as a light source and light intensity has been measured by a silicon photo-diode calibrated for an AM 1.5 spectrum.

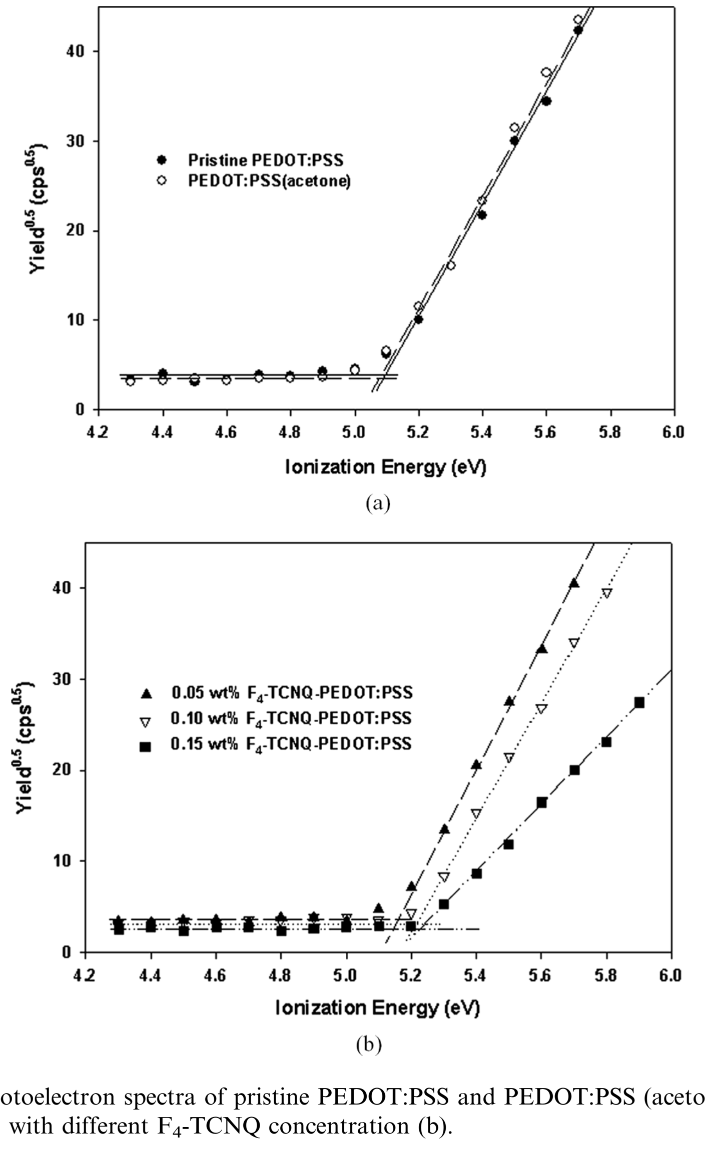


Figure 4. Photoelectron spectra of pristine PEDOT:PSS and PEDOT:PSS (acetone) (a), and PEDOT:PSS with different F_4-TCNQ concentration (b).

Results and Discussion

F_4-TCNQ can be uniformly dispersed in aqueous PEDOT:PSS solution by using acetone as a co-solvent. No turbidity was found in the solution for several days. F_4-TCNQ doped PEDOT:PSS films with a thickness of 35 nm was obtained by spin-coating process. Figure 2 shows the transmission of thin PEDOT:PSS film and various compositions of F_4-TCNQ-PEDOT:PSS films on the glass substrate. As F_4-TCNQ has a higher absorption intensity than PEDOT:PSS in the visible range, a slight decrease of the transmittance was found with the increasing F_4-TCNQ concentrations. Figure 3 shows the conductivity of the F_4-TCNQ-PEDOT:PSS films. As F_4-TCNQ possesses a strong electron accepting property, a significant increase of the conductivity was observed with a small amount of F_4-TCNQ doping in PEDOT:PSS. At the presence of acetone as a co-solvent in aqueous PEDOT:PSS solution, the conductivity of the PEDOT:PSS films slightly increases or maintains almost constant within error range compared to an as-received aqueous PEDOT:PSS solution. Figure 4 shows the photoelectron spectra of the films obtained from as-received PEDOT:PSS, PEDOT:PSS with co-solvent and PEDOT:PSS with different F_4-TCNQ concentrations, and work functions were evaluated using the photoelectron spectra data plot. The work function of the film obtained from PEDOT:PSS with co-solvent was slightly decreased compared to that of the film obtained from as-received PEDOT:PSS (i.e., decreased from 5.09 to 5.08 eV). As F_4-TCNQ doping percent was increased from 0.0 to 0.15 wt% in PEDOT:PSS, the work function was significantly increased from 5.08 to 5.21 eV. F_4-TCNQ is a strong acceptor material and the peripheral electronegative fluorine substituents of the dopant F_4-TCNQ increase its acceptor effect as already known from other classes of molecules [10–12]. This acceptor effect of F_4-TCNQ (electron affinity:5.24 eV) could lead to increasing the work function of F_4-TCNQ doped

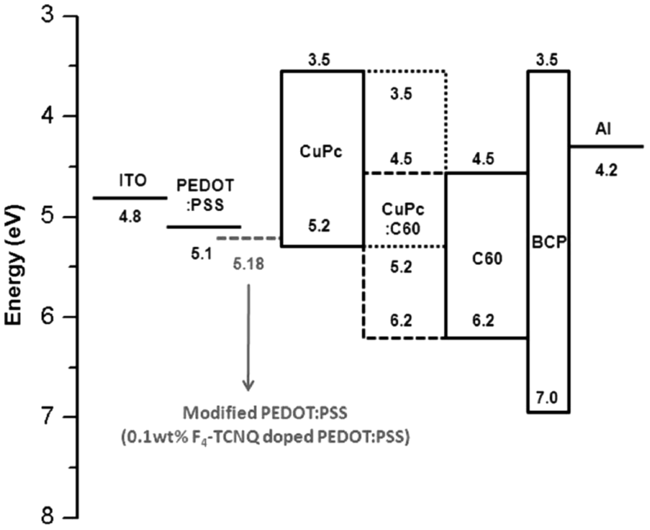
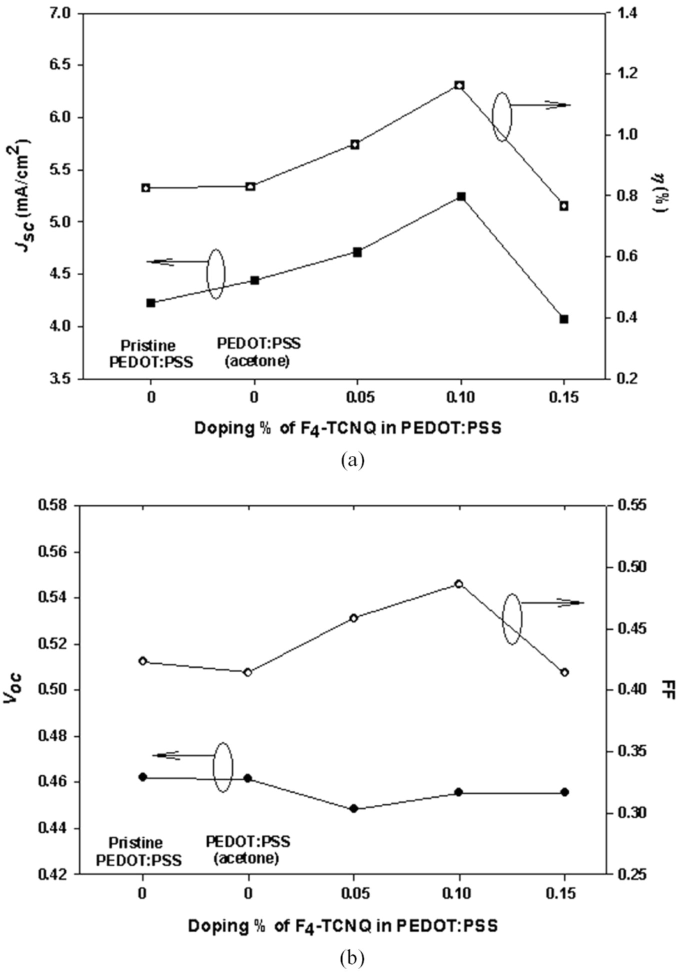


Figure 5. Energy level diagram of the photovoltaic cell for a ITO/F_4-TCNQ-PEDOT:PSS/CuPc/CuPc:C60/C60/BCP/Al device. The references used to build this graft are the following: Ref. 19 and 20.

PEDOT:PSS films. Furthermore, the balance of the carrier mobility of the acceptor and donor should be taken into consideration to improve the device performance. Considering an electron transfer between CuPc and F_4-TCNQ doped PEDOT:PSS films, the work function of F_4-TCNQ doped PEDOT:PSS film should be less than 5.20 eV, as shown in Figure 5, since the ionization energy of CuPc is about 5.20 eV.

Figures 6 and 7 show the photovoltaic responses and current density characteristics for the present devices with different doping amounts of F_4-TCNQ in PEDOT:PSS. The F_4-TCNQ doping concentration was changed from 0.0 to 0.15%. The V_{oc} and FF of the non-doped device were 0.46 and 0.43, respectively. The V_{oc} values maintained almost constant and FF values were gradually increased with increasing the concentration of F_4-TCNQ, and the highest values of J_{sc}, 5.2 mA/cm^2, FF, 0.49, and power conversion efficiency, 1.2%, were obtained at 0.10% of doping concentration of F_4-TCNQ. The current density-voltage was also



(a)

(b)

Figure 6. Photovoltaic response of solar cell devices with different concentration of F_4-TCNQ in PEDOT:PSS layer; J_{sc} and η (a) and V_{oc} and FF (b).

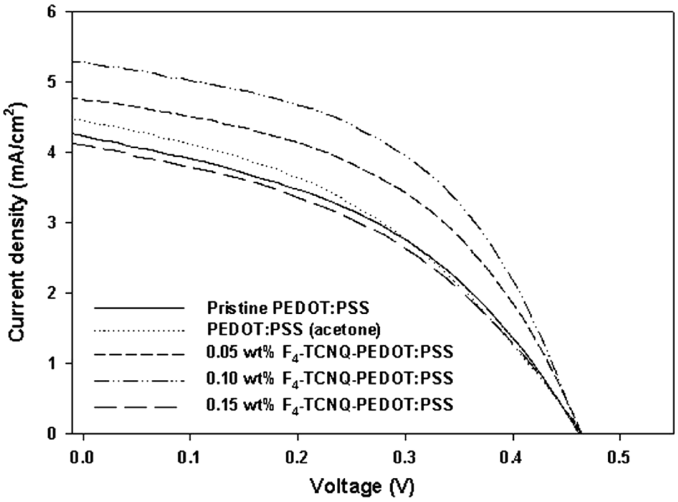


Figure 7. J-V characteristics of the photovoltaic cells with different concentration of F_4-TCNQ in PEDOT:PSS layer.

increased with increasing the concentration of F_4-TCNQ in PEDOT:PSS. However, above 0.10% concentration of F_4-TCNQ, a significant drop in the current density values was observed and the overall device performance, such as V_{oc}, FF, J_{sc}, and power conversion efficiency, was reduced in same manner. This might be due to an unbalanced energy level which could cause an electron transfer blocking between CuPc (5.20 eV) and F_4-TCNQ doped PEDOT:PSS (5.21 eV) films at 0.15% of doping concentration, as shown in Figure 5. Consequently, doping of F_4-TCNQ in p-type layer, PEDOT:PSS, increased the electron transfer through the CuPc and CuPc:C60 layers, since the carrier mobility of the layers was improved by doping of F_4-TCNQ.

Conclusions

Incorporation of F_4-TCNQ into PEDOT:PSS has lead to enhancing the hole conducting ability of PEDOT:PSS, used as the hole conducting layer in organic photovoltaic cells. The good optical transparency was observed in F_4-TCNQ doped PEDOT:PSS films. It has been found that the photovoltaic performance such as J_{sc}, FF and power conversion efficiency was significantly increased with increasing F_4-TCNQ concentration up to 0.10 wt% in PEDOT:PSS since relatively higher work function and better conducting property have been achieved by doping of organic acceptor. The power conversion efficiency is optimized and can be up to 1.20% with 0.1 wt% of F_4-TCNQ in PEDOT:PSS in the organic photovoltaic cell.

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