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Synthesis and Photovoltaic Properties of Polythiophene Incorporating with 3,4-Difluorothiophene Units

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Two polythiophene derivatives using fluorine atoms and hexyl or hexyloxy group as electron-withdrawing and donating substituents have been synthesized. The introduction of fluorine atoms to the polythiophene backbones simultaneously lowers the HOMO and narrows the bandgap, and the stronger electron-donating ability of hexyloxy side chain further reduces the bandgap. As a result, poly[3-hexylthiophene-2,5-diyl-alt-3,4-difluorothiophene] (PHTDFT) shows HOMO and bandgap of −5.31/1.83 eV and poly[3,4-dihexyloxythiophene-2,5-diyl-alt-3,4-difluorothiophene] (PDHOTDFT) shows HOMO and bandgap of −5.14/1.68 eV, both are lower than −4.76/2.02 eV of P3HT. Benefiting from the lower HOMO, PHTDFT:$PC_{61}BM$ (1∶1) polymer solar cells obtain a power conversion efficiency of 1.11% and an impressed open-circuit voltage of 0.79 V under solar illumination AM1.5 (100 mW/cm^2).

Keywords polythiophene derivatives, 3,4-difluorothiophene, polymer solar cell, open-circuit voltage

Introduction

Polymer solar cells (PSCs) based on solution processed bulk-heterojunctions (BHJs) of conjugated polymers have been a world-wide growing field of interest in green energy, due to light weight, flexibility, and low-cost manufacturing, as well as large-area feasibility.[1-6] Among the materials used in PSCs, regioregular poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl-C_{61}-butyric acid methyl ester ($PC_{61}BM$) are the most prominent material system, and the power conversion efficiency (PCE) of the P3HT:$PC_{61}BM$ PSCs can reach around 4%—5% by thermal treatment, solvent annealing, or mixture solvent treatment.[7] In addition, the device performance of the P3HT:$PC_{61}BM$ PSCs is not sensitive to the thickness of active layers in the range of *ca.* 100—300 nm, which is crucial for the production of the PSCs by solution-processing in large area at low cost.[8]

The PCE of P3HT:$PC_{61}BM$ PSCs is limited by the low open-circuit voltage (V_{oc}) values due to the higher-lying highest occupied molecular orbital (HOMO) energy level of P3HT and the relatively lower-lying lowest unoccupied molecular orbital (LUMO) energy level of $PC_{61}BM$, because the V_{oc} of the PSCs is proportional to the difference between the HOMO energy level of the donor polymer and the LUMO energy level of the fullerene derivative.[9,10] In recent years, several new fullerene derivatives with higher-lying LUMO energy levels than $PC_{61}BM$ were synthesized, which significantly increased the V_{oc} of the PSCs based on P3HT and new fullerene derivatives.[11-13]

Another method to improve the V_{oc} is to lower the HOMO energy level of polythiophene by incorporating the electron-withdrawing substituents. By incorporating an ester group, Chen *et al.* reported PCTDT polymer with deep HOMO of −5.27 eV, with a high V_{oc} of 0.68 V.[14] Krebs *et al.* obtained an increased V_{oc} of 0.73 V with P3MHOCT.[15] Similarly, by introducing a substituent carbonitrile group to an alternated copolymer of polythiophene, Guillerez and coworkers reported poly-(3-carbonitrile-3'-hexyl-2,2'-bithiophene) (PD1) with a large V_{oc} of 0.797 V.[16]

In the last few years, fluorine atoms have been used as the most attractive electron-withdrawing group in conjugated polymers for high-efficiency PSCs.[17-19] The fluorine atom with small size could be introduced into the polymer backbone without any deleterious steric effects. Density functional theory calculations predicted a 0.11 eV decreases in the HOMO energy level by adding two fluorine atoms to the benzotriazole unit.[19b] Herein, we report the synthesis of polythiophene derivatives incorporating with 3,4-difluorothiphene unit and

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their photovoltaic performance in bulk heterojunction PSCs. Two polythiophene derivatives using fluorine atoms and hexyl or hexyloxy group as electron-withdrawing and donating substituents have been synthesized. The relationships between molecular structure and photovoltaic property of these polythiophene derivatives are investigated. We find that the introduction of fluorine atoms to the polythiophene backbones simultaneously lowers the HOMO and narrows the bandgap, and the stronger electron-donating ability of hexyloxy side chain further reduces the bandgap. And the deep HOMO energy levels of the polythiophene derivatives lead to an enhanced V_{oc}.

Experimental

Materials and instrumental measurements

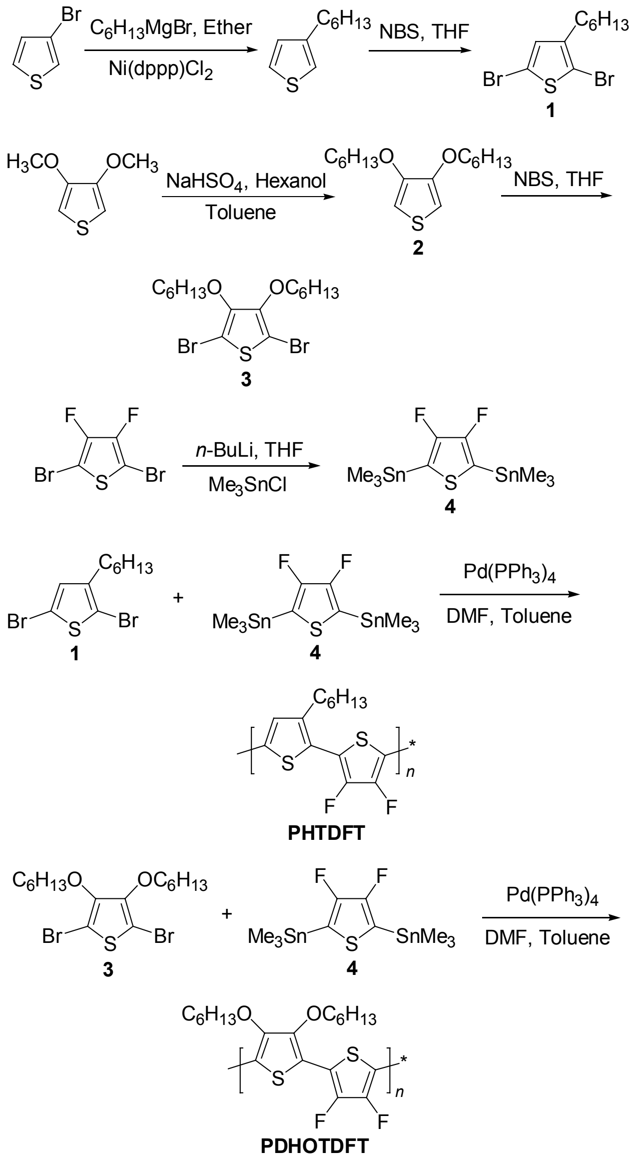
All the solvents were obtained from Sigma-Aldrich and further purified by standard techniques. The reagents were bought from Sigma-Aldrich and used as received. The synthetic routes and molecular structures of the monomers and polymers were shown in Scheme 1. 3-Hexylthiophene and 2,5-dibromo-3,4-difluorothiophene were prepared according to the previously reported procedures.[20,21]

^1H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 MHz at ambient temperature using TMS as reference. Molecular weights and distributions were determined by gel permeation chromatography (GPC) on a Waters 1500 HPLC Pump equipped with UV-vis detector (model Waters2489) working at 270 nm, and a set of Waters Styragel columns (HT3, and HT4, 7.8×300 mm). GPC measurements were carried out at 35 ℃ using THF as eluent at a flow rate of 1.0 mL/min, and polystyrene as the standard. The UV-vis spectra were evaluated on a Varian Cary 5000 UV-vis spectrometer at wavelength from 300 to 800 nm. The electrochemical cyclic voltammetry was conducted on a CHI 410B Electrochemical Workstation with Pt disk coated with the polymer film, Pt plate, and Ag/Ag^+ electrode as working electrode, counter electrode, and reference electrode respectively in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) acetonitrile solution. The electrochemical potential was calibrated against Fc/Fc^+.

Fabrication of polymer solar cells

Polymer solar cells with the structure of ITO/PEDOT:PSS/polymer:$PC_{61}BM$/Ca (20 nm)/Al (150 nm) were fabricated under conditions as follows: After spin-coating a 50 nm layer of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) onto a pre-cleaned indium-tin oxide (ITO)-coated glass substrates, the polymer (10 mg/mL)/$PC_{61}BM$ blend solution in dichlorobenzene was spin-coated. The thickness of the active layer was about 60 nm. After thermal annealed for 15 min under argon, the devices were completed by evaporating Ca/Al metal electrodes with an area of 3.14 mm^2 defined by metal masks. All devices were characterized with a Keithley 2400 source measure unit under ambient conditions, and the typical illumination intensity was 100 mW/cm^2 (AM 1.5G Oriel solar simulator).

Scheme 1 Synthetic routes for the monomers and polymers



Synthesis of the monomers and polymers

2,5-Dibromo-3-hexylthiophene (1) To an ice-cooled solution of 3-hexylthiophene (1.68 g, 10.0 mmol) in anhydrous *N*,*N*-dimethylformamide (DMF) (20.0 mL) was added dropwise a solution of *N*-bromosuccinimide (NBS, 3.56 g, 20.0 mmol) in anhydrous DMF (20.0 mL). After stirred overnight at room temperature, the mixture was then quenched with water, extracted with ether (20 mL×3). The organic phase was combined and washed with water and brine, dried over anhydrous magnesium sulfate, concentrated and purified by column chromatography using *n*-hexane as eluent to give a colorless oil (2.6 g, 80% yield). ^1H NMR (400 MHz, $CDCl_3$) δ: 6.78 (s, 1H), 2.51 (t, J=7.5 Hz, 2H), 1.62—1.47 (m, 2H), 1.39—1.30 (m, 6H), 0.89 (t, J=6.6 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ: 143.15, 131.11, 110.45, 108.07, 31.71, 29.69, 29.63, 28.93, 22.71, 14.21.

3,4-Dihexyloxythiophene (2) A solution of 3,4-dimethoxythiophene (1.44 g, 10.0 mmol), hexanol (4.08 g, 40.0 mmol) and $NaHSO_4$ (0.12 g, 1.0 mmol) in anhydrous toluene (10 mL) was refluxed overnight at 110 ℃. After the mixture was cooled to room temperature, 20 mL dichloromethane (DCM) was added. The resulting mixture was washed with an aqueous solution of sodium hydrogencarbonate and brine, dried over anhydrous magnesium sulfate, concentrated and purified by column chromatography using *n*-hexane/ DCM (10 : 1) as eluent to give a colorless oil (1.70 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.16 (s, 2H), 3.98 (t, J=6.7 Hz, 4H), 1.88—1.75 (m, 4H), 1.46—1.33 (m, 12H), 0.91 (t, J=6.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.76, 97.08, 70.72, 31.71, 29.15, 25.79, 22.71, 14.12.

2,5-Dibromo-3,4-dihexyloxythiophene (3) In the absence of light, *N*-bromosuccinimide (NBS, 1.78 g, 10.0 mmol) was added in portions to a solution of 3,4-dihexyloxythiophene **2** (1.42 g, 5.0 mmol) in anhydrous DMF (10 mL). The mixture was stirred at room temperature for 3 h, then poured into water, extracted with DCM (10 mL×3). The organic phase was washed with water and brine, dried over anhydrous magnesium sulfate, concentrated and purified by column chromatography using *n*-hexane/DCM (10 : 1) as eluent to give a colorless oil (1.33 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 4.05 (t, J=5.6 Hz, 4H), 1.79—1.66 (m, 4H), 1.48—1.33 (m, 12H), 0.89 (t, J= 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.81, 95.35, 74.11, 31.71, 30.06, 25.68, 22.75, 14.16.

3,4-Difluoro-2,5-bis-trimethylstannanyl-thiophene (4) *n*-BuLi in hexane (2.4 mol•L^{-1}, 9.2 mL, 22.0 mmol) was added dropwise in a solution of 2,5-dibromo-3,4-difluoro-thiophene (2.78 g, 10.0 mmol) in THF (50 mL) at −78 ℃ under argon, and the mixture was stirred at −78 ℃ for 30 min. The Me_3SnCl in THF (1.0 mol•L^{-1}, 21.0 mL, 21.0 mmol) was added dropwise. The resulting mixture was stirred at −78 ℃ for 1 h, then allowed to warm to room temperature and poured into water, extracted with ether (20 mL×3). The organic phase was washed with water and brine, dried over anhydrous magnesium sulfate, concentrated and purified by column chromatography using *n*-hexane as eluent to afford product as a white solid (3.56 g, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.39 (s, 18H).

General polymerization procedure In a 100 mL Schlenk flask, 1.0 mmol of dibromothiophene monomer, 0.41 g (1.0 mmol) of 3,4-difluoro-2,5-bis-trimethylstannanyl-thiophene (**6**) and 50 mg (0.044 mmol) of tetrakis(triphenylphosphine)palladium(0) were added. The flask was purged three times with argon. 16.0 mL of degassed toluene and 4.0 mL of degassed DMF were added, and the mixture was heated to 120 ℃ for 48 h. Then the reactant mixture was cooled to room temperature. The crude polymer was precipitated in methanol. After washing with methanol and *n*-hexane using a Soxhlet apparatus, the product was recovered with chloroform. The product was finally dried under vacuum for 1 d.

Poly[3-hexylthiophene-2,5-diyl-alt-3,4-difluorothiophene] (PHTDFT) Following the general polymerization procedure, 326 mg (1.0 mmol) of 2,5-dibromo-3-hexylthiophene (**1**) was reacted for 48 h. The polymer was recovered with chloroform as a red dark powder (40 mg, 14 % yield).

Poly[3,4-dihexyloxythiophene-2,5-diyl-alt-3,4-difluorothiophene] (PDHOTDFT) Following the general polymerization procedure, 442 mg (1.0 mmol) of 2,5-dibromo-3,4-dihexyloxythiophene (**5**) was reacted for 48 h. The polymer was recovered with chloroform as a red dark powder (75 mg, 19% yield).

Results and Discussion

Characterization of polymers

The two polythiophene derivatives are soluble in common organic solvents such as THF and dichlorobenzene. Calibration against the polystyrene standard, PHTDFT gives a number-average molecular weight (M_n) of 2691 and a weight-average molecular weight (M_w) of 2929 with a polydispersity (PDI) of 1.09. Introducing hexyloxy chains into the polymer main chain could increase the solubility. Thus the PDHOTDFT has a M_n of 3861 and a M_w of 5439 with a PDI of 1.41. The molecular weights of these two polymers are similar to their derivatives.[16,22] The low nucleophilicity of 3,4-difluoro-2,5-bis-trimethylstannanylthiophene caused by two strong electro-negative fluorine substituent group could result in low reactivity toward nucleophilic attack in the transmetallation reaction step in the Stille cross-coupling reactions.[23]

Optical properties

The UV-vis absorption spectra of PHTDFT and PDHOTDFT solutions in chloroform are shown in Figure 1. In the visible region, one absorption peak is observed, which could be attributed to the π-π* transition of the conjugated polymer main chains. In solutions, the peak of absorption spectrum of PHTDFT is at about 430 nm, while the PDHOTDFT appeared at 515 nm that shows a red shift of about 85 nm, which is due to the stronger electron-donating ability of hexyloxy side chain of PDHOTDFT than hexyl side chain of PHTDFT.[24]

Figure 1 also shows the UV-vis absorption spectra of the polymer films on quartz plate. The optical data including the absorption edge wavelength (λ_{onset}, abs) and the optical band gap (E_g^{opt}) of films are summarized in Table 1. In comparison with the absorption spectra of the polymer solutions in chloroform, the visible absorption of the films shows a red shift.[25,26] The optical band gaps (E_g^{opt}) are 1.77 and 1.90 eV for PDHOTDFT and PHTDFT, respectively.

Table 1 Optical and electrochemical properties of polymers

Polymer	$\lambda_{\text{max, sol.}}$/nm	$\lambda_{\text{onset, film}}$/nm	E_g^{opt} /eV	φ_{ox}/V (vs. Ag/Ag$^+$)	E_{HOMO}/eV	φ_{red}/V (vs. Ag/Ag$^+$)	E_{LUMO}/eV	E_g^{ec} /eV
PHTDFT	430	650	1.90	0.87	−5.31	−0.96	−3.48	1.83
PDHOTDFT	515	700	1.77	0.70	−5.14	−0.98	−3.46	1.68
P3HT[a]					−4.76		−2.74	2.02

[a] Data from ref 25.

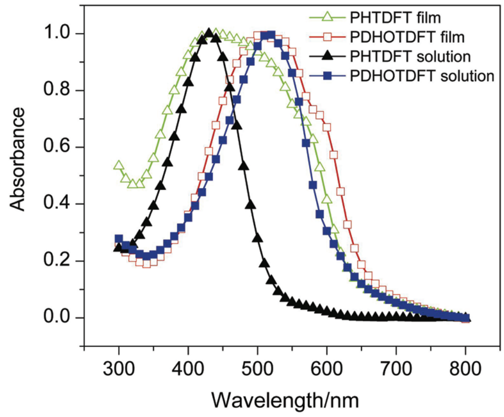


Figure 1 UV-vis absorption spectra of PDHOTDFT and PHTDFT in chloroform solutions and thin film on fused quartz.

Electrochemical properties

The electrochemical properties of PHTDFT and PDHOTDFT are investigated by cyclic voltammetry (CV). The cyclic voltammograms of the polymer film on platinum plates are shown in Figure 2. All measurements are calibrated using ferrocene (Fc) value of +0.36 eV as the standard. The HOMO energy levels can be calculated by an equation of $\text{HOMO}=-(E_{\text{onset,ox}}-E_{\text{Fc}}+4.8)$ (eV), and the LUMO energy levels by an equation of $\text{LUMO}=-(E_{\text{onset,red}}-E_{\text{Fc}}+4.8)$ (eV).[27] From the values of $E_{\text{onset,ox}}$ and $E_{\text{onset,red}}$, the HOMO and the LUMO as well as the electrochemical bandgaps (E_g^{ec}) of the polymers can be estimated by the following equations:

$$E_{\text{LUMO}}=-(E_{\text{onset,red}}+4.44)\ \text{(eV)}$$
$$E_{\text{HOMO}}=-(E_{\text{onset,ox}}+4.44)\ \text{(eV)}$$
$$E_g^{\text{ec}}=\text{e}\ (E_{\text{onset,ox}}-E_{\text{onset,red}})\ \text{(eV)}$$

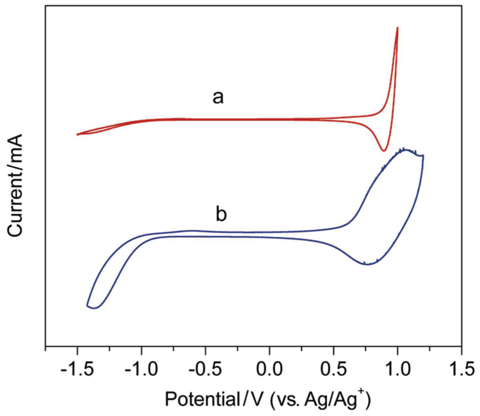


Figure 2 Cyclic voltammograms of PHTDFT (a) and PDHOTDFT (b) film on platinum plates in an acetonitrile solution of 0.1 mol/L Bu_4NPF_6 at a sweep rate of 0.1 V/s.

Bandgaps of the two polymers are a little smaller than that of P3HT, although both the HOMO and LUMO dropped by some extent (Table 1). This phenomenon indicated that the HOMO energy level can be efficiently reduced by introducing fluorine atoms to the polymer backbones. It was observed that PDHOTDFT has a higher HOMO value (−5.14 eV) than that of PHTDFT (−5.31 eV), which is in accordance with the previous study on polythiophenes that conjugated polymer with alkoxy group as a substituent usually exhibited a higher HOMO level than alkyl-substituted polymer.[28]

Photovoltaic properties

To study the photovoltaic properties of PHTDFT and PDHOTDFT, PSCs are fabricated with a device structure of ITO/PEDOT:PSS (50 nm)/polymer:$PC_{61}BM$/Ca (20 nm)/Al (150 nm). In the photovoltaic devices, the polymer is used as electron donor while $PC_{61}BM$ is used as electron acceptor.

Firstly, PSCs based on PHTDFT and $PC_{61}BM$ blends with different ratios are fabricated. Then the device performances of PHTDFT and $PC_{61}BM$ blend with the best ratio (1∶1) at different thermal annealing temperatures are investigated. The highest efficiency is obtained in PSCs with PHTDFT:$PC_{61}BM$ blend (1∶1) and thermal annealing under 100 ℃. Further increasing annealing temperature to 160 ℃, the deterioration of morphology of active layers induced lower V_{oc} and lower efficiency.[29] For PDHOTDFT, photovoltaic performances are also investigated with different blend ratios and thermal annealing. However, we observe a significant decrease in the PCE for the cells based on PDHOTDFT:$PC_{61}BM$ blend with thermal annealing (see supporting information Table 1S). The current density-voltage (J-V) curves of the optimized PSCs based on PHTDFT and PDHOTDFT under the illumination of AM1.5, 100 mW/cm^2 are shown in Figure 3. The PCE of the PSCs based on PHTDFT and PDHOTDFT are 1.11% and 0.78%, respectively. The corresponding V_{oc}, short-circuit current (J_{sc}), fill factor (FF), and PCE of the devices based on the two polymers are listed in Table 2. The J_{sc} of the device based on the PDHOTDFT is larger than that of the device based on PHTDFT, benefiting from the broad response range of PDHOTDFT in visible range, as showed in Figure 1. The V_{oc} of the devices based on PHTDFT are 0.79 V. In comparison with the device based on P3HT (V_{oc} is *ca.* 0.6 V), the V_{oc} of the device based on PHTDFT increased by *ca.* 0.2 V. The higher V_{oc} is expected from the lower HOMO energy level of PHTDFT, which originated from the strong

Table 2 The corresponding V_{oc}, short-circuit current (J_{sc}), fill factor (FF), and PCE of PSCs based on PHTDFT and PDHOTDFT

Polymer	Annealing temperature/℃	J_{sc}/(mA•cm^{-2})	V_{oc}/V	FF/%	PCE/%
PHTDFT:PC$_{61}$BM (1 ∶ 1)	100	2.31	0.79	60.8	1.11
PDHOTDFT:PC$_{61}$BM (1 ∶ 1)	—	3.27	0.57	42	0.78

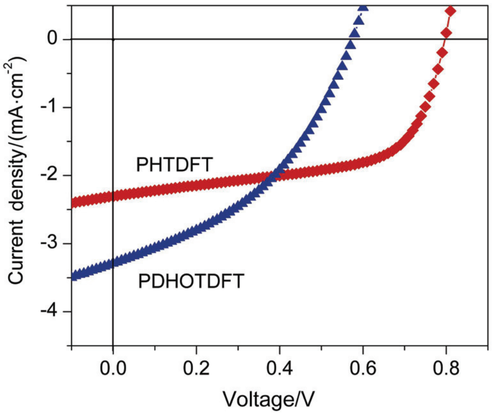


Figure 3 *J-V* curves of the PSC devices based on PHTDFT and PDHOTDFT under illumination of AM 1.5G, 100 mW/cm^2.

electro-negative fluorine substituent group on the polymer main chain.

Conclusions

Two new polythiophene derivatives incorporating with 3,4-difluorothiphene units, PHTDFT and PDHOTDFT, are designed and synthesized, and used as donor material in PSCs. PHTDFT and PDHOTDFT exhibited lower HOMO and narrow bandgap than that of P3HT. Benefiting from the lower HOMO, PHTDFT: PC$_{61}$BM (1 ∶ 1) polymer solar cells obtain a power conversion efficiency of 1.11% and an impressed open-circuit voltage of 0.79 V under solar illumination AM1.5 (100 mW/cm^2).

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