A Novel Acrylonitrile Derivative Having Photovoltaic Performance

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Abstract: A new acrylonitrile derivative, *2-(4-bromophenyl)-3-{5-[2-cyano-2-phenylethenyl]furan-2-yl}acrylonitrile (***BPCPFA, 3***)* which is a potential material for application in organic solar cells, was synthesized by a three-step reaction. The structures of the molecules synthesized in these steps were characterized by using various spectral analyses. **BPCPFA** was investigated as an electron acceptor molecule in next generation organic solar cells. Theoretical prediction and experimental studies for photovoltaic performance were also performed. Based on these results, it is concluded that **BPCPFA** with extended conjugated system has good and promising photovoltaic performance with V_{oc} value as 0.96 V.

Keywords: Conjugated systems; nitriles; organic solar cells; photovoltaics.

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INTRODUCTION

Organic photovoltaics (OPVs) are an encouraging field to produce energy as a renewable energy source. The simple processing, cost-effective fabrication, and device flexibility of organic solar cells make them superior as compared to the inorganic solar cells. Recently, the most popular and efficient way of fabricating organic solar cells is to use the bulk heterojunction concept in which an electron donor and an acceptor is blended in a solution and cast as a film from this solution. The development of bulk heterojunction organic solar cells has shown a fascinating increase in the power conversion efficiency [1-4].

Despite all this increase, their power conversion efficiency is still low as compared to inorganic solar cells. The most efficient organic solar cells make use of small organic molecules and conjugated polymers in their structure. Most of the small molecules and conjugated polymers used in photovoltaics are mostly p-type (donor) materials [5, 6]. In this area, the number of materials exhibiting n-type (acceptor) properties is very restricted and among acceptor type molecules the most well-known molecules are fullerenes. For example [6, 6]-phenyl C_{61} butyric acid methyl ester (PCBM) is a fullerene derivative which has excellent acceptor characteristics. Unfortunately, PCBM also has some disadvantages such as air degradation and cost intensive synthesis [7, 8]. The need for new acceptor materials for organic photovoltaics is growing rapidly. Consequently, the importance of these materials increases dramatically day by day.

We have synthesized a novel acceptor organic molecule which contains furan ring with electron-withdrawing cyano groups **(BPCPFA)** and investigated its photovoltaic properties. Until recently, various organic small molecules have been synthesized for solar cells. However, most of these molecules have commonly triphenylamine-based structure and are often symmetric [9]. The molecular structure containing heterocyclic system of these type diarylacrylonitriles has been synthesized to investigate their capacity in solar cells as acceptor elsewhere [7, 10-13].

In this study, photovoltaic properties of a new compound was thoroughly investigated. We achieved comparably a higher V_{oc} as compared to the reference device employing P3HT (poly(3-hexylthiophene-2,5-diyl)) and PCBM blends.

MATERIALS AND METHODS

All reactions were carried out under nitrogen atmosphere. The solvents were purchased from Merck and dried by standard methods (using anhydrous CaO and distillation). The reagents were used without further purification from commercial suppliers.

The FT-IR spectra were collected on a Perkin Elmer, Spectrum One Bv 5.0 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Unity Inova Spectrometer (500 MHz) using $CDCl_3$. The LC-MS spectra were measured on an Agilent 1200 Infinity HPLC with Agilent 6460 spectrometer.

Melting points of synthesized compounds were determined with Gallenkamp melting point apparatus in open capillaries.

As substrates, ITO (indium tin oxide) glass sheets of 1.5 cm x 1.5 cm, from Kintec Company, Hong kong which has a sheet resistance < 12 $\Omega.cm^{-2}$ were used. The ITO was patterned by etching with an acidic mixture of $HCl:HNO_3:H_2O$ (4.6:0.4:5) for 30 min. The part of the substrate which forms the contact was covered with a scotch tape to prevent etching. The tape was removed after etching and the substrate was then cleaned using distilled water, acetone and isopropanol in an ultrasonic bath, respectively as described elsewhere [7].

The active layer with 1:0.5 wt ratio was prepared by blending 10 mg of P3HT and 5 mg of compound **3** (**BPCPFA**) in 1 mL of chlorobenzene (CB) and also blends for active layer with 1:1 wt ratio was prepared by dissolving 10 mg of P3HT and 10 mg of **3 (BPCPFA)** in 1 mL of chlorobenzene (CB).

For the organic bulk heterojunction solar cells, poly(3,4-ethylenedioxythiophene)–poly(styrenesulfonate) (PEDOT:PSS) was deposited on to the ITO coated glass substrate by spin coating at 2000 rpm in air. The PEDOT:PSS layers were annealed in a furnace at 150 °C for 4 minutes. Active layers of P3HT:CPCPFA were spin-coated onto PEDOT:PSS films at 800 rpm in a glovebox. For some of the devices, thermal annealing of the active layer was done on a hot plate at 120 °C for 3 minutes. Finally, 100 nm Al was thermally evaporated as top contact.

All current–voltage (I–V) characteristics of the PV devices were measured (using a Keithley 2400) under nitrogen in a dry glove box just after production. Abet solar simulator, simulating AM1.5 conditions, was used as the excitation source with an input power of 100 mW/cm^2 white-light illumination.

The power conversion efficiencies of the organic solar cells were calculated according to the following equation:

$$\eta_{AM\ 1.5}\ (\%) = \left(\frac{P_{out}}{P_{\text{in}}}\right) x\ 100 = \frac{FF\ V_{oc}\ J_{sc}}{P_{in}}\ x\ 100 \qquad \text{(Eq. 1)}$$

The percentage efficiency, ηAM 1.5, is given by the ratio of the power output (P_{out}), to the power input from the solar simulator (P_{in}, 100mW/cm^2). The output power of a solar cell under illumination is the product of the fill factor (FF), the open-circuit voltage V_{oc} (V) and the current density under short circuit conditions J_{sc} (mA/cm^2). The fill factor is obtained using the following equation:

$$FF = \frac{V_{mpp}\ J_{mpp}}{V_{oc}\ J_{sc}} \qquad \text{(Eq. 2)}$$

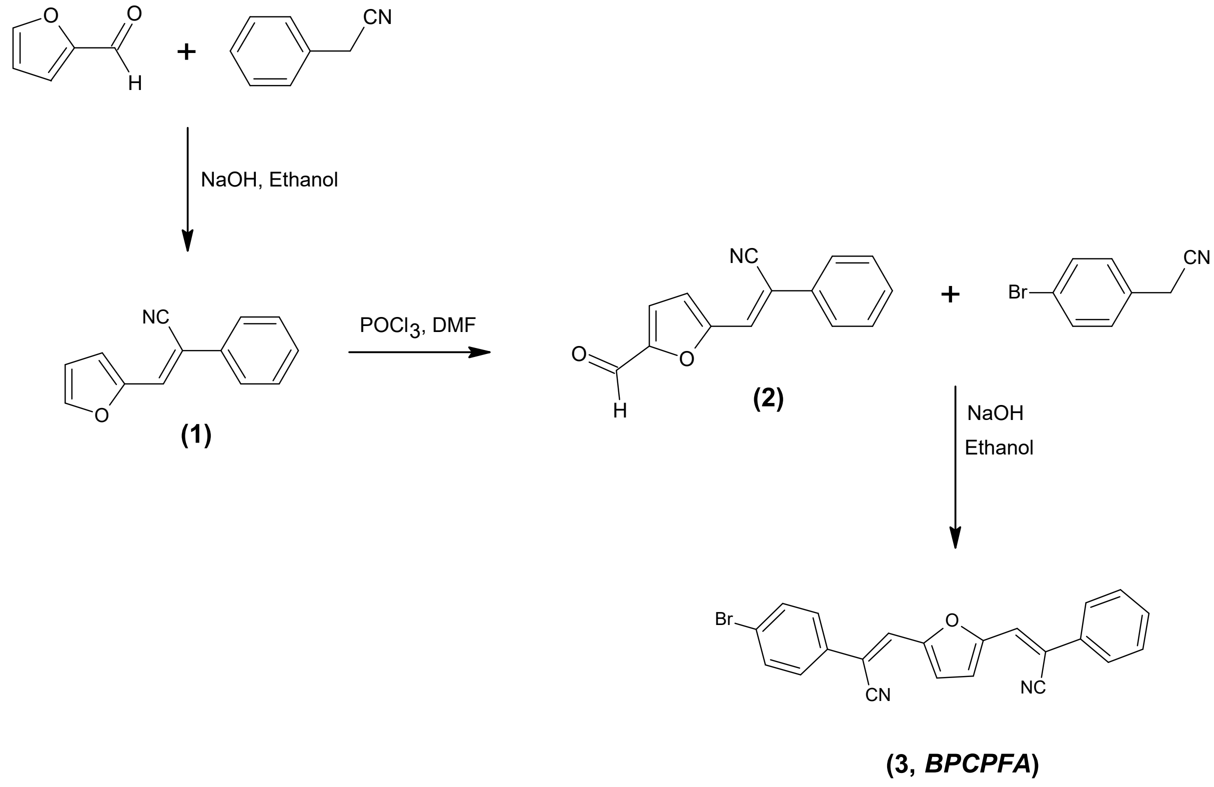
where the maximum power point of the product of the voltage and the current density (V_{mpp} and J_{mpp}) is divided by the product of the open-circuit voltage and the short circuit current.

The current–voltage curves (*J–V*) of the photovoltaic devices were created by a Keithley 2400 under nitrogen atmosphere.

Synthesis

The compound **3 (BPCPFA)** studied in this paper was prepared via a three-step procedure (Scheme 1).

The nitrile derivatives (**1-3)** were obtained by the reaction of appropriate starting materials and characterized by using FT-IR, ^{1}H NMR, ^{13}C NMR, and LC-MS spectral data. All data supported the structures of target molecules (Figure 1-4, *see SI*).



Scheme 1. Synthesis of compounds (**1-3)**.

*Synthesis of 2-phenyl-3-(furan-2-yl)acrylonitrile (**1**)* [7]

Furan-2-carbaldehyde (1 mmol) and phenylacetonitrile (1 mmol) were dissolved in dry ethanol (10 mL). After that, sodium hydroxide (0.1 mmol) was added and stirred for 5 min at room temperature under nitrogen atmosphere. The precipitated yellow solid was filtered, washed with ethanol, and recrystallized in $CHCl_3$ to give pure product **1** as light yellow crystals [14]. Yield: 97%, mp 86-88 °C. FT-IR (ATR) v, 3098, 3057, 3045, 2214, 1683, 1595 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 6.55 (m, 1H, furan), 7.32 (brd, *J*= 7.0 Hz, 1H, furan), 7.53 (brs, 1H, =CH), 7.58 (brd, *J*= 3.2 Hz, 1H, furan), 7.64 (m, 3H, ArH), 8.12 (d, *J*= 8.0 Hz, 2H, ArH); ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 112, 120, 128, 129, 130, 134, 144, 147, 148, 163, 172. LC-MS m/z: 196 [M]$^+$ (calculated for $C_{13}H_9NO$, 195.22).

*Synthesis of 2-phenyl-3-(5-formylfuran-2-yl)acrylonitrile (**2**)* [7]

The freshly distilled DMF (3 eq) and POCl$_3$ (5 eq) was stirred for 30 min at 0°C, under nitrogen. Compound **1** (0.5 g, 1.49 mmol) in CH_2Cl_2 (5 mL) was added to the mixture and stirred for 12 h at room temperature [15]. The obtained solid was collected by filtration and purified by column chromatography on silica gel using ethyl acetate/hexane (5:1). A dark yellow solid of compound **2** was obtained. Yield: 83%, mp 127-129 °C. FT-IR (ATR) ν, 3098, 3062, 3032, 2222, 1667, 1596 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.38 (d, *J*= 7.0 Hz, 1H, furan), 7.47 (brd, *J*= 3.2 Hz, 1H, furan), 7.49 (m, 3H, ArH), 7.50 (brs, 1H, =CH), 7.67 (d, *J*= 8.0 Hz, 2H, ArH), 9.73 (s, 1H, -CHO); ^{13}C NMR (125 MHz, CDCl$_3$) δ (ppm) 113, 115, 117, 122, 126, 129, 130, 132, 133, 152, 154, 178. LC-MS m/z: 224 [M]$^+$ (calculated for $C_{14}H_9NO_2$, 223.23).

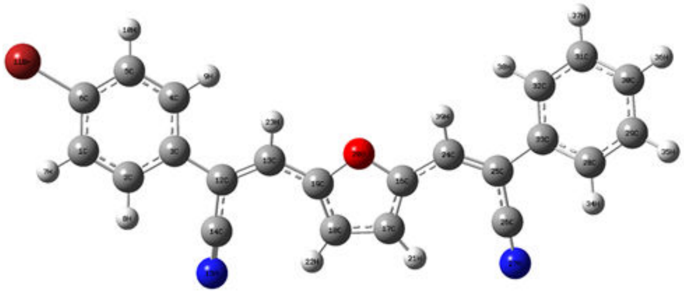
*2-(4-Bromophenyl)-3-{5-[2-cyano-2-phenylethenyl]furan-2-yl}acrylonitrile (**3,** **BPCPFA**)*

The compound **3 (BPCPFA)** synthesized from compound **2** and 4-bromophenylacetonitrile starting materials according to the same procedure with compound **1** [7, 15]. Light-orange solid. Yield: 97%, mp 159-161°C. FT-IR (ATR) ν, 3088, 3051, 3029, 2209, 1675, 1596 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$): δ (ppm) 7.42 (s, 2H, 2 x -C=CH), 7.43-7.49 (m, 5H, ArH), 7.55-7.62 (m, 4H, ArH), 7.69 (d, *J*= 7.2 Hz, 2H, ArH). ^{13}C-NMR (125 MHz, CDCl$_3$): δ (ppm) 109, 111, 117, 118, 126, 127, 129, 130, 136, 152. LC-MS m/z: 402 [M]$^+$ (calculated for $C_{22}H_{13}BrN_2O$, 401.25).

RESULTS AND DISCUSSION

Theoretical calculation of HOMO-LUMO

HOMO and LUMO energies of the compound **3** have been calculated. The calculations were saved using Gaussian 09 W software [16] by DFT/B3LYP method with 6-31 G(d) basis set. Optimized molecular structure and energy of the **BPCPFA** are given in Figure 5.



E= -98.032 KeV

Figure 5. Optimized molecular structure and energy of ***BPCPFA***.

HOMO-LUMO energies are crucial in order to explain the chemical reactivity and stability of molecule. Determination of the HOMO-LUMO level alignment between the donor and acceptor is crucial to designate whether there will be an efficient charge transfer or not [17, 18]. The HOMO-LUMO energy gap of **BPCPFA** is shown in Figure 6. HOMO-LUMO energy band for new compound **3** is 2.83 eV, so it is possible that charge transfer interaction may easily occur in the molecule.

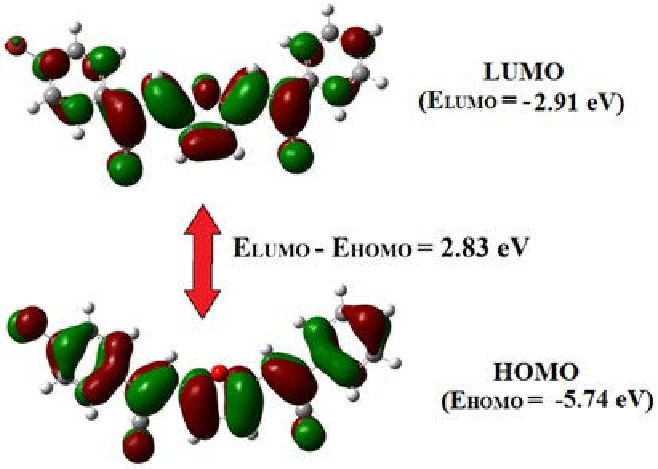


Figure 6. HOMO-LUMO energy diagrams for compound **3**, ***BPCPFA*.**

The theoretical HOMO-LUMO levels of P3HT are -4.32 eV and -2.3 eV, whereas the values of PCBM are -5.66 eV and -3.02 eV, respectively [19]. In calculations performed for **BPCPFA**, the HOMO and LUMO energies were calculated to be -5.74 eV and -2.91 eV. It can be concluded that since the LUMO level of P3HT lies above the **BPCPFA**, and there is an energy difference of 0.61 eV between their LUMOs which is more than 0.3 eV, a charge transfer can be possible between P3HT and **BPCPFA**. Therefore, P3HT was evaluated as a donor whereas **BPCPFA** was generated as an acceptor in the organic solar cells.

Photovoltaic Studies

Photovoltaic performance of the devices employing active layers of P3HT:BPCPFA with different weight ratios (1:0.5 and 1:1 wt) have been studied. A reference device in which no BPCPFA employed was also studied to understand whether BPCPFA has an acceptor role in the device. As can be seen from Figure 7a, devices comprising of 1:0.5 wt donor acceptor ratio showed a short-circuit current density (J_{sc}) of 0.124 mA/cm^2, an open-circuit voltage (V_{oc}) of 960 mV and a fill factor (FF) of 0.24 was calculated which led to a power conversion efficiency (PCE) of 0.029 %.

We achieved a J_{sc} of 0.206 mA/cm^2 and a V_{oc} of 958 mV, and an FF of 0.26 which led to a PCE of 0.051 % for the devices containing of 1:1 wt donor acceptor ratio (Figure 7b).

There is an ongoing debate on the nature of the open-circuit voltage in literature, however V_{OC} value is known to be proportional to the difference between the HOMO of the donor and the LUMO of the acceptor. In the best case, we achieved a V_{OC} of 0.960 V.

V_{OC} value can be calculated by the following equation [20, 21]:

$$V_{OC} = (1/e)[(E_{donor}\text{HOMO}) - (E_{acceptor}\text{LUMO})] - 0.3\ \text{V} \qquad \text{(Eq. 3)}$$

Figure 7c displays the *J-V* curves of the reference P3HT device (J_{sc} = 0.017 mA/cm^2, V_{OC} =105 mV and FF = 0.28).

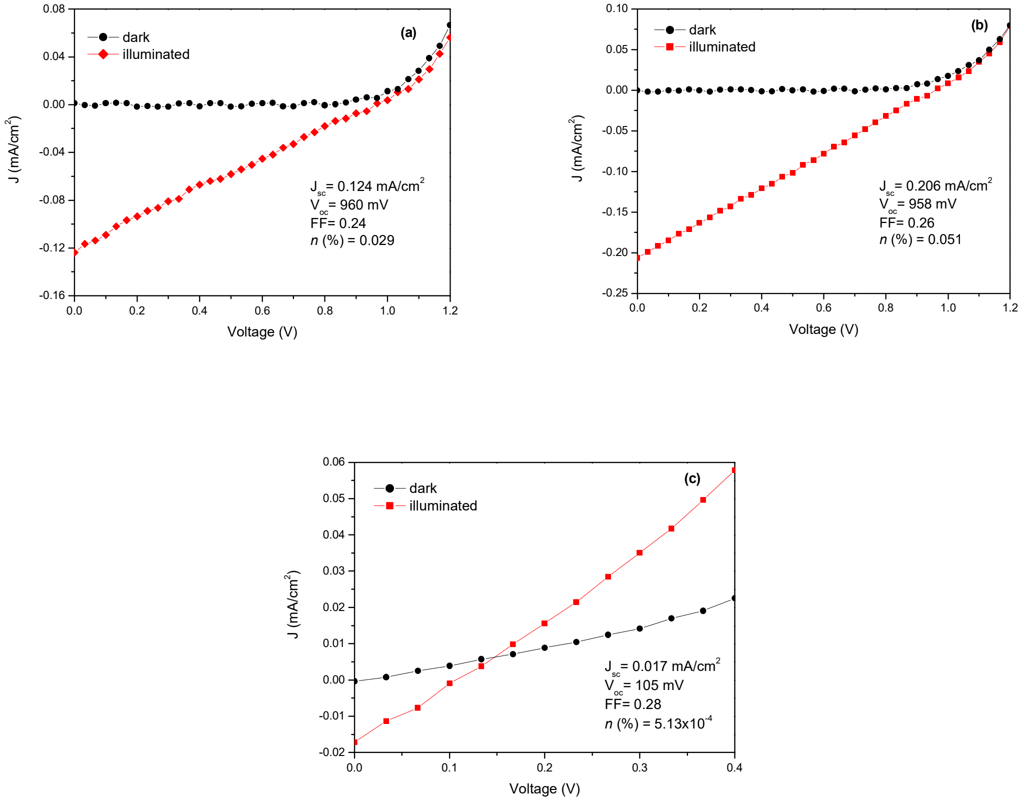


Figure 7. *J*–*V* curves of (a) devices with active layers of 1:0.5 donor–acceptor ratio, (b) 1:1 donor–acceptor ratio, (c) *J*–*V* curves of a reference device.

Briefly, the performance of the device created by using **BPCPFA** is approximately 7 times more than the performance of created by using P3HT reference.

CONCLUSIONS

In conclusion, a new diarylacrylonitrile derivative **(BPCPFA)** was used as an electron acceptor in organic solar cells and its synthetic and device performance characteristics were fully investigated. The photovoltaic performance of this compound was investigated using both theoretical and experimental techniques. The acceptor type molecules for photovoltaic use are off great interest. Polymer or small molecule acceptors have several advantages such as good absorption in the visible region and a higher LUMO energy level than PCBM, which in turn leads to a high open-circuit voltage (V_{OC}). We achieved a V_{OC} of 960 mV, which is higher than that of the conventional bulk heterojunction organic solar cells comprising of P3HT and PCBM.

The offset of HOMO and LUMO levels between donor and the acceptor is very important to get efficient charge transfer. The offset of HOMO-LUMO energy levels should be almost 0.3 eV. The theoretical HOMO-LUMO energy levels of **BPCPFA** are very close to that of PCBM which is most used as an electron acceptor materials in organic photovoltaics.

Based on all the data of our study, further studies will be carried on by changing the device parameters and molecular structure.

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Türkçe Öz ve Anahtar Kelimeler

Fotovoltaik Performans Gösteren Yeni bir Akrilonitril Türevi

Çiğdem Yörür-Göreci*,Mehmet Kazici, Sinem Bozar, Zulal Demir, Abdullah Toraman, Fatih Ongul, Abid Ali, Serap Güneş

Öz: Yeni bir akrilonitril türevi olan 2-(4-bromofenil)-3-{5-[2-siyano-2-feniletenil]furan-2-il}akrilonitril (**BPCPFA, 3**) bileşiğinin organik güneş pillerinde uygulanma potansiyeli vardır ve üç kademeli bir tepkimeyle sentez edilmiştir. Bu adımlar sırasında sentezlenen moleküllerin yapıları çeşitli spektral analizler kullanılarak karakterize edilmiştir. **BPCPFA** yeni nesil organik güneş pillerinde elektron alıcı molekül olarak incelenmiştir. Teorik tahminler ve fotovoltaik performans için deneysel çalışmalar da yürütülmüştür. Bu sonuçlara dayanarak, **BPCPFA**'nın uzamış konjuge sistemiyle iyi ve ümit vaat eden bir fotovoltaik performans (V_{oc} = 0,96 V) gösterdiği sonucuna varılmıştır.

Anahtar kelimeler: Konjuge sistemler; nitriller; organik güneş pilleri; fotovoltaikler.

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