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Symmetrical molecules of low band gap with a central spacer connected via ether bond with terminal 4-nitro- α -cyanostilbene units: Synthesis and application for bulk heterojunction solar cells

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ABSTRACT

Two new soluble and symmetrical molecules **M1** and **M2** of low band gap with a central spacer which was connected at both sides via ether bond with terminal 4-nitro- α -cyanostilbene units were synthesized. The spacer of **M1** and **M2** consisted of dihexyloxyphenylene and n-hexylene, respectively. Their long-wavelength absorption maximum was at 590-640 nm. The thin film absorption onset for both molecules was located at 742 nm which corresponds to an optical band gap of 1.67 eV. We have fabricated bulk heterojunction (BHJ) photovoltaic devices using these molecules as donor and PCBM as acceptor. We have investigated the solvent vapor treatment effect of these blends on their morphology and photovoltaic properties. We found that the overall power conversion efficiency (PCE) for the devices based on the solvent vapor treated M1:PCBM and M2:PCBM blends is 3.05% and 1.90%, respectively, higher than those of pristine blends. This increase of PCE has been attributed to the increase in surface roughness of the blend and better balance in charge transport. The PCE has been further increased up to 3.57% and 2.42% with the thermally annealed solvent treated M1:PCBM and M2:PCBM blend, respectively. This increase of PCE may be attributed to the enhanced crystallinity of the blend and reduction of the space charge effect, improving the charge transport and collection efficiency.

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1. Introduction

There is a strong continuing interest in the development of polymer based photovoltaic (PV) devices. Bulk heterojunction (BHJ) polymer PV devices have proven to be the most efficient thus far [1]. Solar cells prepared from polymer and organic materials are attractive for their potential in low cost in manufacturing large-area, lightweight, and flexible devices. These materials offer the possibility to be used by solution processing like printing, doctor blading, or spray deposition. Certain reviews for advanced materials and processes of polymer solar cells have recently been reported [2]. The key steps that occur in organic based PV devices are: light absorption to form an exciton, separation of the exciton into holes and electrons, and movement of the generated holes and electrons to the electrodes. There are clearly many factors that affect each of these steps including the optical density of the polymer and its morphology. To achieve separation of the exciton, the BHJ approach requires two materials of different electron and hole affinities to be mixed. This has been achieved using polymer blends [3-5] but the most



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common approach has been to blend the polymer with [6,6]-phenyl-C61-butyric methyl ester (PCBM), a soluble C60 derivative [1,6].

The overall power conversion efficiency (PCE) has been steadily improving from an initial 1% via a blend of poly[2methoxy-5-(30,70-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV) with PCBM [7] to an impressive \sim 5% achieved by poly(3-hexylthiophene) (P3HT):PCBM via extensive morphology optimization [8-10]. In order to further improve the efficiency of BHJ polymer solar cells, the research community is searching for new polymers. From the materials perspective, these donor polymers should not only have a low band gap, in order to increase the short circuit current (J_{sc}) , but also bear a low energy level of the highest occupied molecular orbital (HOMO) to improve the open circuit voltage (V_{oc}) [11]. Typically, a low band gap polymer is designed via a "donor-acceptor" (D-A) approach, which is to incorporate electron-rich and electron-deficient moieties in the polymer backbone. The low band gap is mainly caused by the intramolecular charge transfer between donor and acceptor units [12]. Currently, state of the art polymer based BHJ solar cells have reached PCEs of more than 6% [13] and 6.7% [14] have been reported for single and tandem solar cells, respectively. However, these numbers are still significantly lower than the critical efficiencies of 10–15% [15].

In parallel efforts, organic solar cells (OSCs) based on small-molecules with vacuum evaporating interpenetrating multilayer structures have also reached PCEs as high as 5-6% [16]. Small-molecule donor materials can also form useable BHJ solar cells by solution processing, although it is more challenging to obtain high-quality films. The highest reported efficiencies for such devices have remained low (PCEs range from 0.3% to \sim 3.0%) relative to solution-processed solar cells using polymeric donor materials (\sim 5%). Small-molecule materials, however, offer advantages over polymeric materials in terms of ease of synthesis and purification, which greatly improve fabrication reproducibility, as well as possessing a greater tendency to self assemble into ordered domains, which leads to high charge carrier mobilities [17]. Small-molecules do not suffer from batch to batch variations, broad molecular-weight distributions, end-group contamination, or difficult purification methods, which can be significant problems for polymeric materials. These considerations make small-molecules a promising class of donor material for BHJ solar cell applications [18-26]. Solution-processed small-molecules, which have been used for PV cells, have recently been reviewed [27]. Efficient BHJ PV solar cells based on symmetrical $D-\pi$ -A- π -D organic dye molecules [28], squaraine [29,24], phthalocyanines [30,31], oligothiophene with dialkylated diketopyrrolopyrrole [32,33], 2-vinyl-4,5-dicyanoimidazole (vinazene) [34,35] and starshaped molecules have very recently been reported [36-40]. The highest PCE reported to date for solar cells using solution-processable small-molecules is 3.0% [32].

On the other hand, cyano-poly(*p*-phenylenevinylene) (CN-PPV) and its derivatives with cyanovinylene moieties are one of the most important conjugated polymers with high electron affinity and promising materials used in polymeric light emitting diodes and polymeric PV devices [41–46]. Various low band gap small-molecules and poly-

mers carrying 4-nitro- α -cyanostilbene units have been synthesized in our laboratory and used for BHJ solar cells [47] and dye-sensitized solar cells [48] with enhanced efficiency. In continuation of this research line, herein we describe the synthesis and characterization of two new symmetrical molecules M1 and M2 of low band gap with common structural segments. Both molecules contained a central spacer which was connected at both sides via ether bond with terminal 4-nitro- α -cyanostilbene units. The two ether bonds are expected to increase the flexibility of the molecules. Moreover, their aliphatic moieties render these molecules very soluble in common organic solvents thus allowing the facile preparation of thin films by spin casting. The molecules were successfully synthesized by a reaction sequence the last step of which included the condensation of a kye-dialdehyde with 4-nitrobenzylcyanide. We have used M1 and M2 as electron donor along with PCBM as electron acceptor for BHJ active layer for the fabrication of organic PV devices. The PCE for the devices based on pristine M1:PCBM and M2:PCBM blends, is 1.67% and 1.05%, respectively. We have investigated the effect of solvent vapor treatment of blend on the PV response of the BHI devices and found that the PCE has been increased up to 3.05% and 1.90% for M1:PCBM and M2:PCBM blends, respectively. This improvement of PCE has been attributed to the increase in hole mobility and surface roughness, leading to better charge separation and collection efficiency. The PCE has been further increased up to 3.57% and 2.42% after thermal annealing of the solvent vapor treated M1:PCBM and M2:PCBM blends, respectively.

2. Experimental

2.1. Reagents and solvents

4-Nitrobenzylcyanide was synthesized from the nitration of benzyl cyanide with concentrated nitric and sulfuric acid [49]. It was recrystallized from ethanol. 4-Hydroxybenzaldehyde was recrystallized from distilled water. *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were dried by distillation over CaH₂. All other reagents and solvents were commercially purchased and were used as supplied.

2.2. Preparation of compounds

2.2.1. 1,4-Bis(p-formylphenoxymethyl)-2,5-bis(hexyloxy) benzene (3)

A flask was charged with a mixture of **2** (0.1650 g, 0.355 mmol), 4-hydroxybenzaldehyde (0.1042 g, 0.853 mmol), K₂CO₃ (0.15 g, 1.08 mmol) and acetonitrile (25 mL). The mixture was stirred and refluxed for 12 h under N₂. It was subsequently concentrated under reduced pressure. Water was added to the concentrate and then it was extracted with dichloromethane. The organic layer was dried (Na₂SO₄) and concentrated to afford **3** (0.1478 g, yield 76%).

FT-IR (KBr, cm⁻¹): 2930, 2870, 2854 (C–H stretching); 1684 (carbonyl of formyl); 3050, 1602, 1506, 1466 (aromatic); 1246, 1210, 1162 (ether bond).

¹H NMR (CDCl₃) ppm: 9.90 (s, 2H, formyl); 7.79 (m, 4H, aromatic ortho to formyl); 6.96–6.85 (m, 6H, aromatic

ortho to oxygen); 5.14 (s, 4H, OCH₂Ph); 3.96 (m, 4H, OCH₂(CH₂)₄CH₃); 1.81 (m, 4H, OCH₂CH₂(CH₂)₃CH₃); 1.37 (m, 12H, O(CH₂)₂(CH₂)₃CH₃); 0.91 (t, 6H, O(CH₂)₅CH₃).

Anal. Calcd. for $C_{34}H_{42}O_6$: C, 74.70; H, 7.74. Found: C, 74.32; H, 7.40%.

2.2.2. Molecule M1

A flask was charged with a solution of **3** (0.1478 g, 0.270 mmol) and 4-nitrobenzylcyanide (0.0876 g, 0.540 mmol) in ethanol (20 mL). Sodium hydroxide (0.20 g, 5.00 mmol) was added to this solution. The reaction mixture was stirred for 1 h at room temperature under N_2 and then it was concentrated under reduced pressure. Water was added to the concentrate and **M1** precipitated as a dark green solid. It was recrystallized from ethanol/water (0.15 g, yield 66%).

FT-IR (KBr, cm⁻¹): 2922, 2852 (C–H stretching); 2170 (cyano); 1510, 1346 (nitro); 3075, 1600, 1454 (aromatic); 1258, 1162, 1106 (ether bond); 1016 (*trans*-vinylene bond).

¹H NMR (CDCl₃) ppm: 8.11 (m, 4H, aromatic ortho to nitro); 7.72 (s, 2H, cyanovinylene); 7.65 (m, 4H, aromatic meta to nitro); 7.26 (m, 4H, aromatic meta to oxygen); 6.88–6.85 (m, 6H, aromatic ortho to oxygen); 5.15 (s, 4H, OCH₂Ph); 3.97 (m, 4H, OCH₂(CH₂)₄CH₃); 1.80 (m, 4H, OCH₂CH₂(CH₂)₃CH₃); 1.38 (m, 12H, O(CH₂)₂(CH₂)₃CH₃); 0.90 (t, 6H, O(CH₂)₅CH₃).

Anal. Calcd. for $C_{50}H_{50}N_4O_8$: C, 71.92; H, 6.04; N, 6.71. Found: C, 71.53; H, 6.17; N, 6.90%.

2.2.3. Molecule M2

This molecule was synthesized in 70% yield from the reaction of dialdehyde **4** with a double molar amount of 4-nitrobenzylcyanide in ethanol in the presence of NaOH according to the procedure described for **M1**.

FT-IR (KBr, cm⁻¹): 2936, 2860 (C–H stretching); 2160 (cyano); 1510, 1346 (nitro); 3073, 1600 (aromatic); 1250, 1174, 1106 (ether bond); 1010 (*trans*-vinylene bond).

¹H NMR (CDCl₃) ppm: 8.12 (m, 4H, aromatic ortho to nitro); 7.74 (s, 2H, cyanovinylene); 7.66 (m, 4H, aromatic meta to nitro); 7.32 (m, 4H, aromatic meta to oxygen); 6.80 (m, 4H, aromatic ortho to oxygen); 3.92 (m, 4H, OCH₂); 1.68 (m, 4H, OCH₂ CH₂); 1.27 (m, 4H, O(CH₂)₂ CH₂).

Anal. Calcd. for $C_{36}H_{30}N_4O_6$: C, 70.35; H, 4.92; N, 9.12. Found: C, 69.94; H, 4.80; N, 9.28%.

2.3. Characterization methods

IR spectra were recorded on a Perkin–Elmer 16PC FT-IR spectrometer with KBr pellets. ¹H NMR (400 MHz) spectra were obtained using a Brucker spectrometer. Chemical shifts (δ values) are given in parts per million with tetra-methylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectrograde THF. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

The electrochemical cyclic voltammetry was conducted with Pt disk, Pt wire and Ag/Ag⁺ electrode as working electrode, counter electrode, and reference electrode, respectively, in a 0.1 mol/L tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) acetonitrile solution. The **M1** or **M2** films for the electrochemical measurements were coated from THF solution containing **M1** or **M2**.

2.4. Device fabrication and characterization

Organic solar cell devices with the structure ITO/PED-OT:PSS/M1 or M2:PCBM (1:1)/Al were fabricated as follows: After spin-coating of 40 nm layer of poly (3,4ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT: PSS) onto a pre-cleaned ITO coated glass substrates and baking at 80 °C for 30 min, a 80 nm M1:PCBM or M2:PCBM blend layer in THF solution was deposited on the top of the PEDOT:PSS layer by controlled spin-coating rate. Finally, an Al electrode (50 nm) was deposited on the top of the active BHJ layer through the thermal evaporation method. The effective area of the each device is 0.08 cm². For the solvent treatment, the spin coated blends were transferred into a jar filled with THF. Pre-thermal annealing of the solvent treated active layers was carried out at 120 °C for 2 min on the hot plate before the deposition of the Al electrode. The devices based on pure M1 or M2 were also fabricated having structure ITO/PEDOT:PSS/M1 or M2/Al.

Current–voltage (*J–V*) characteristics of the PV devices were measured using a computer controlled Keithley 238 source meter in dark as well as under illumination intensity of 100 mW/cm². A xenon light source (Oriel, USA) was used to give a simulated irradiance of 100 mW/cm² (equivalent to AM1.5 irradiation) at the surface of the device. The hole only device having ITO/PEDOT:PSS/**M1** or **M2**:PCBM/Au configuration using as cast the thermally annealed active layers, were fabricated and *J–V* characteristics in dark at room temperature, were recorded to estimate the hole mobility.

The incident photon to current efficiency (IPCE) of the devices was measured by illuminating the device with a xenon light source using monochromator and measuring the resulting photocurrent with a Keithley electrometer under short circuit conditions according to the following expression:

 $IPCE(\%) = 1240 J_{sc} / \lambda P_{in}$

where J_{sc} is the short circuit photocurrent and λ and P_{in} are the wavelength and illumination intensity of the incident light, respectively.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 outlines the four-step reaction sequence applied for the synthesis of the target molecule **M1**. In particular, **1** [50] and **2** [50] were synthesized by reported procedures. The reaction of **2** with 4-hydroxybenzaldehyde in a mol ratio 1:2 afforded dialdehyde **3**. This reaction took place in acetonitrile in the presence of K_2CO_3 . Finally, the Knoevenagel condensation [51] of **3** with a double molar amount of 4-nitrobenzylcyanide in ethanol in the presence of NaOH yielded **M1**. It is well known that this type of condensation forms double bonds which possess mainly *trans*-conformation [52]. The facile synthesis of the other target molecule **M2** was achieved in only two steps according to Scheme 2. Specifically, 4-hydroxybenzaldehyde reacted



Scheme 1. Synthesis of molecule M1.



Scheme 2. Synthesis of molecule M2.



Fig. 1. FT-IR (top) and ¹H NMR in CDCl₃ solution (bottom) spectra of molecule M1.

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with 1,6-dibromohexane to afford dialdehyde **4** [53]. The latter was subsequently condensed with 4-nitrobenzylcyanide to give **M2**. Both molecules were obtained in relatively high yields (66–70%) as dark green solids which were purified by recrystallization from ethanol/water. The two hexyloxy side chains of **M1** and the hexylene spacer of **M2** enhanced the solubility of these molecules. Particularly, both molecules were readily soluble in common organic solvents such as THF, dichloromethane, chloroform, acetone and toluene. Thin films of these molecules could be obtained by spin casting from the solutions despite their monomer nature.

Since the molecules have comparable chemical structures, their spectra showed certain common features. Fig. 1 presents the FT-IR and ¹H NMR spectra of **M2** as an example. The IR spectrum displayed characteristic absorption bands at 2936, 2860 (C–H stretching of hexylene); 2160 (cyano); 1510, 1346 (nitro); 3073, 1600 (aromatic); 1250, 1174, 1106 (ether bond) and 1010 cm⁻¹ (*trans*-vinylene bond). The latter appeared at longer wavelength than usual *trans*-vinylene bonds (970–960 cm⁻¹) owing to the substitution by the electron-withdrawing cyano group. On the other hand, the ¹H NMR spectrum of **M2** showed upfield signals at 8.12 and 7.74 ppm assigned to the aromatic ortho to nitro and the cyanovinylene respectively. The other aromatic resonated at 7.66–6.80 ppm, while the aliphatic at 3.92–1.27 ppm.

3.2. Photophysical and electrochemical properties

Fig. 2 depicts the UV-vis absorption spectra of molecules in dilute (10^{-5} M) THF solution and thin film, which were normalized with respect to the long-wavelength absorption. Table 1 summarizes the photophysical and electrochemical characteristics of both molecules. Their absorption curves were broad and extended approximately up to 750 nm. This behavior is attributable to the terminal 4-nitro- α -cyanostilbene units as it has been well established in our previous publications [47,48]. The longwavelength absorption maximum ($\lambda_{a,max}$) was located at 590–640 nm. The $\lambda_{a,max}$ of **M2** was red-shifted relative to that of M1 in both solution and thin film. However, both molecules displayed the same thin film absorption onset at 742 nm which corresponds to an optical band gap (E_{σ}^{opt}) of 1.67 eV. This value of E_{g}^{opt} conforms to those of other related materials [47,48].

Electrochemical cyclic voltammetry has been widely employed to investigate the redox behavior of organic materials and to estimate their HOMO and LUMO energy levels [54]. Fig. 3 shows the cyclic voltammograms of **M1** and **M2** films on Pt electrode in a 0.1 mol/L Bu₄NPF₆–acetonitrile solution. The results of the electrochemical measurements are listed in Table 1. It can be seen from Fig. 3 that there are reversible *n*-doping/depoping (reduction/ reoxidation) and *p*-doping/depoping processes in both negative and positive potential range, respectively. The onset oxidation potential (E_{ox}) for **M1** and **M2** is 0.5 V and 0.7 V vs. Ag/Ag⁺, respectively. The lower value of the oxidation potential for **M1** indicates higher electron donating ability of **M1** as compared to **M2**. In the reduction potential region, the onset reduction potential (E_{red}) is -1.21 V and



Fig. 2. Normalized absorption spectra of molecules in THF solution (top) and thin film (bottom).

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Optical and electrochemical properties of molecules.

Molecule	M1	M2
$\lambda_{a,max}^{a}$ in solution (nm)	590	607
$\lambda_{a,max}^{a}$ in thin film (nm)	622	640
Thin film absorption onset (nm)	742	742
$E_{\rm g}^{\rm optb}$ (eV)	1.67	1.67
$E_{\text{onset}}^{\text{ox}}$ (V)	0.5	0.7
$E_{\text{onset}}^{\text{red}}$ (V)	-1.2	-1.0
HOMO (eV)	-5.2	-5.4
LUMO (eV)	-3.5	-3.7
$E_{\rm g}^{\rm elc}$ (eV)	1.7	1.7

^a $\lambda_{a,max}$: the long-wavelength absorption maxima from the UV-vis spectra in THF solution or in thin film.

^b E_{g}^{opt} : optical band gap determined from the absorption onset in thin film.

 $^{\rm c}$ $E_{\rm g}^{\rm el}$: electrochemical band gap determined from cyclic voltammetry.

-1.0 V vs. Ag/Ag⁺ for **M1** and **M2**, respectively. From the E_{ox} and E_{red} of molecules **M1** and **M2**, their HOMO and



Fig. 3. Cyclic voltammetry data of M1 and M2.

LUMO energy levels as well as their energy gaps were calculated according to equations:

 $LUMO = -q(E_{red} + 4.7) (eV)$ $HOMO = -q(E_{ox} + 4.7) (eV)$

where the units of E_{ox} and E_{red} are V vs. Ag/Ag⁺. The HOMO and LUMO values of these molecules are included in Table 1. It can be seen that the HOMO energy level of **M2** (-5.4 eV) is lower than that of **M1** (-5.2 eV). The LUMO level of **M2** (-3.7 eV) is higher than that of **M1** (-3.5 eV). However, the electrochemical band gap $(E_g^{\text{el}})(1.7 \text{ eV})$ is almost the same for both molecules. The E_g^{el} estimated from the electrochemical data is in good agreement with the E_g^{opt} estimated from the thin film absorption onset. The HOMO and LUMO levels of the PCBM were also estimated from the electrochemical data and were found to be -6.5 eV and -4.1 eV, respectively. The difference between the LUMO level of **M1** or **M2** and PCBM is about 0.6 eV and 0.4 eV, respectively, which indicates that the combination of **M1** or **M2** as donor with PCBM as an acceptor can be used for efficient BHJ organic PV devices.

3.3. Electrical and photoelectrical properties of M1 and M2

The *I–V* characteristics of the ITO/PEDOT:PSS/M1 or M2/ Al devices in dark and under illumination are shown in Fig. 4. In these curves, the forward bias corresponds to the positive and negative voltage applied to PEDOT:PSS/ ITO and Al electrode, respectively. It can be seen from these figures that the I-V characteristics show a rectification effect. The HOMO level of PEDOT:PSS (-5.2 eV) is very close to the HOMO level of both M1 and M2. Therefore, this electrode behaves almost as an Ohmic contact for hole injection from the PEDOT:PSS into the HOMO of M1 and M2 in their respective devices. However, the LUMO level of both M1 and M2 is very far from the work function of the Al (-4.3 eV) and forms the Schottky barrier for the electron injection from the Al into the LUMO level of molecules. Hence, the rectification effect observed in the dark *I–V* characteristics is due to the formation of Schottky barrier at the Al-M1 or Al-M2 interfaces.

The charge carrier mobility of the PV materials is also an important factor which influences the performance of organic solar cells. We have measured the hole mobilities of these molecules using the hole only devices with ITO/PEDOT:PSS/**M1** or **M2**/Au structure using the SCLC model [55]. The *J*-*V* characteristics of the devices were plotted as $\ln[Jd^3/(V_{app} - V_{bi})]$ vs. $[(V_{app} - V_{bi})/d]^{0.5}$, and the hole mobilities of **M1** and **M2** calculated from the intercept of the corresponding lines are 2.3×10^{-6} and 5.1×10^{-6} cm²/Vs for **M2** and **M1**, respectively.

The PV parameters, i.e. short circuit current (J_{sc}), open circuit voltage (V_{oc}), fill factor (FF) and PCE are summarized in Table 2. It can be seen from this table that the values of J_{sc} and PCE are higher for the device based on **M1** as compared to **M2**. This is attributed to the higher hole mobility of **M1** as compared to **M2**, since the E_g^{opt} and the absorption spectra



Fig. 4. Current-voltage characteristics of the devices based on pure M1 and M2 in dark (a) and under illumination (b).

 Table 2

 Summary of photovoltaic parameters of the ITO/PEDOT:PSS/M1 or M2/Al devices.

Active material	Short circuit current (<i>J</i> _{sc}) (mA/cm ²)	Open circuit voltage (V_{oc}) (V)	Fill factor (FF)	Power conversion efficiency (PCE) (%)
M1	0.62	0.69	0.41	0.17
M2	0.47	0.72	0.40	0.13

of both molecules are identical. As the HOMO level of **M1** is very close to the HOMO level of PEDOT:PSS, the better hole collection in the device based on **M1** as compared to **M2**, may also be the reason for the higher PCE.

3.4. Photovoltaic properties of BHJ devices

The BHJ OSCs were fabricated with a structure of ITO/ PEDOT:PSS/**M1** or **M2**:PCBM (1:1)/Al, where **M1** or **M2** were used as electron donor and PCBM was used as electron acceptor. Fig. 5 shows the *J*–*V* characteristics of the devices and Table 3 lists the corresponding PV parameters (J_{sc} , V_{oc} , FF and PCE) of the devices under illumination intensity of 100 mW/cm². It can be seen from Table 3 that the device based on the as cast **M1**:PCBM blend shows better PV response, having PCE of 1.67% as compared to 1.05% for the device based on the as cast **M2**:PCBM blend. The IPCE spectra of the devices (Fig. 6) show similar shape to the absorption spectra of the respective blends employed in the devices. This indicates that the visible light absorbed by the **M1**:PCBM or **M2**:PCBM photoactive layer in respec-



Fig. 5. Current-voltage characteristics of the devices based on pristine **M1**:PCBM and **M2**:PCBM blend under illumination intensity of 100 mW/ cm².

Table 3

Summary of photovoltaic parameters of BHJ devices, using layer with different processing conditions.

Active material	Short circuit current (J _{sc}) (mA/cm ²)	Open circuit voltage (V _{oc}) (V)	Fill factor (FF)	Power conversion efficiency (PCE) (%)
M1:PCBM ^a M1:PCBM ^b M1:PCBM ^c M2:PCBM ^a M2:PCBM ^b M2:PCBM ^c	3.76 6.4 7.12 2.38 4.15 5.16	0.93 0.90 0.93 0.98 0.95	0.48 0.53 0.54 0.45 0.48	1.67 3.05 3.57 1.05 1.90 2.42

^a Pristine blend.

^b Solvent vapor treated blend.

^c Thermally annealed solvent treated blend.



Fig. 6. IPCE spectra of BHJ devices based on pristine M1:PCBM and M2:PCBM blends.



Fig. 7. Absorption spectra of solvent vapor treated M1:PCBM and M2:PCBM blends.

tive devices contributes to the J_{sc} . The maximum of IPCE for the as cast **M1**:PCBM and **M2**:PCBM based devices are about 55% and 42%, respectively at their absorption peak. The IPCE values are consistent with the higher values of J_{sc} and PCE of the **M1**:PCBM blend based organic solar cell.

The J_{sc} is directly related to the product of absorbed photons and external quantum efficiency (EQE) [27]. Since the optical absorption of both **M1**:PCBM and **M2**:PCBM is almost the same, light absorption cannot be the factor for increased J_{sc} and PCE of the device based on **M1**:PCBM as compared to **M2**:PCBM. We assume that the difference in EQE of the devices is responsible for the higher photocurrent of the **M1**:PCBM blend. The EQE is determined by three processes: (i) migration/diffusion of photogenerated excitons towards the D/A interface, (ii) excitons dissociation and charge separation at the D/A interfaces, and (iii) collection of charge carrier at the electrodes. The process (i) depends on the nanoscale phase separation between the donor and acceptor components used in the BHJ active layer. It can be seen from the AFM images (Figs. 9 and 10)



Fig. 8. Current–voltage characteristics of the devices based on THF treated **M1**:PCBM and **M2**:PCBM blend under illumination intensity of 100 mW/cm².

that the surface roughness is higher for M1:PCBM as compared to M2:PCBM, which indicates better nanoscale phase separation in M1:PCBM blend. Therefore, we assume that the contribution of EQE from the process (i) is higher for M1:PCBM. For process (ii) a sufficient large energy difference between the LUMO of the donor and acceptor material is required for ultra-fast photoinduced charge transfer. This difference is higher for M1:PCBM as compared to M2:PCBM blend. Photoinduced charge transfer is comparatively faster in the former blend, resulting in higher EQE for the device based M1:PCBM blend. Process (iii) depends on the percolated path for electrons and holes in BHJ active layer, mobility of electron and hole, and on the position of HOMO and LUMO level of the donor and acceptor materials, respectively, relative to the work function of anode and cathode. The HOMO level of M1 is closer to the HOMO level of PEDOT:PSS indicating higher hole mobility for M1, which results in more efficient hole collection. Therefore, processes (i-iii) are responsible for the improved J_{sc} and PCE of the device based on M1:PCBM as compared to M2:PCBM.

Generally, the performance of the organic BHJ PV devices can be improved by controlling the morphology of the BHJ active layer, because efficient photoinduced charge generation, transport and collection of charge carriers at each collecting electrode crucially depend on the nanometer scale morphology of the films [56]. The crystallization of the organic materials improves the light harvesting property by extending the conjugation length and increases the charge carrier mobility, which is the limiting factor for the balance transport of the electrons and holes dissociated from the bound excitons. The increase in the PCE via thermal annealing is attributed to modified nanoscale morphology, enhanced crystallization of blend and improved transport of charges. It has also been reported that self-organization of organic material occurs not only under thermal annealing but also in proper ambience. Li et al. [9] and Zhao et al. [57] reported efficient PV cells based on P3HT/PCBM blend by controlling the growth rate of the active layer from solution to solid state. We have investigated the effect of thermal annealing, and combining solvent vapor treatment and thermal annealing on the PCE of PV devices based on M1:PCBM and M2:PCBM blends.

Fig. 7 shows the UV–vis absorption spectra of the solvent vapor treated M1:PCBM and M2:PCBM blends. For the untreated M1:PCBM blend film, the M1 absorption peak is located at 620 nm with an absorption onset at 742 nm. Compared to the pristine M1:PCBM blend film, the absorption peak of the solvent treated M1:PCBM blend film shifted towards longer wavelength region and became much stronger in this region. In addition, the absorption spectra of the solvent treated M1:PCBM blend shows one vibronic absorption shoulder at 680 nm, which is attributed to an enhanced conjugation length and more ordered structure of M1. As the solvent molecules can penetrate into the film and increase the space between the molecular chains, the chains become mobile and self-organization can occur to form the ordering.

Fig. 8 shows the J-V characteristics of the devices under 100 mW/cm² white light illumination with THF treatment. The PV parameters for these PV devices are summarized in Table 3. It can be seen that the J_{sc} of the PV devices with THF vapor treatment increases to 6.4 mA/cm² and



Fig. 9. AFM images of M1:PCBM as cast (a) and solvent treated (b) films.



Fig. 10. AFM images of M2:PCBM as cast (a) and thermally annealed (b) films.

(b)

4.15 mA/cm² for M1:PCBM and M2:PCBM based devices respectively, which is a twofold increase compared to the as produced PV device. The overall PCE of the devices based on the solvent treated M1:PCBM and M2:PCBM has been increased up to 3.05% and 1.90%, respectively. This improvement is attributed to the self-organization of M1 or M2 induced by solvent vapor treatment which enhances the optical absorption and the hole transport. The PCE of the BHJ devices with THF treatment blends are higher than that of pristine blends. The J_{sc} of the organic BHJ PV devices is directly related to the product of light absorption by the photoactive blend used in the device, exciton diffusion, charge separation and charge collection efficiency. As it can be seen from the absorption spectra of the solvent vapor treated blends, the absorption coefficient has been increased as compared to the as cast blend films and also red-shifted. This indicates that more light is absorbed by the solvent vapor treated blends which generated more excitons in the photoactive blend. It is also observed that the IPCE spectra of the devices resemble the absorption spectra of the corresponding blend used in the device. This indicates that the J_{sc} is mainly attributed to the excitons generated because of the absorption of photons in M1 or M2. The value of the IPCE is consistent with the values of *J*_{sc}. The IPCE is higher for the devices based on the solvent vapor treated blends as compared to the pristine blends, which is consistent with the increased values of I_{sc} .

The nanoscale morphology of the blend films has been investigated by the atomic force (AFM) experiment. Figs. 9 and 10 show the AFM images of the as cast and solvent vapor treated blend films. For the as cast films, an rms surface roughness of 4.2 nm and 3.2 nm, for M1:PCBM and M2:PCBM, respectively is observed. The solvent vapor treated films are much rougher that the as cast films. The solvent vapor treated M1:PCBM and M2:PCBM films show rms roughness of 7.6 nm and 5.6 nm, respectively at $5 \,\mu m \times 5 \,\mu m$ scan sizes. The roughness is considered to be a signal of M1 or M2 chains self-organization and phase separation [57]. The increase of the roughness of the blend films after solvent vapor treatment is because of the M1 or M2 chains, self organize into ordered structure after solvent vapor treatment. The higher surface roughness of the blends support the increase in the phase separation of M1:PCBM or M2:PCBM after solvent vapor treatment. The increased phase separation leads to an increase in the D/A interfacial area for efficient charge separation, resulting in higher J_{sc} and PCE for BHJ PV devices based on the solvent vapor treated blend films.

The $V_{\rm oc}$ values of the devices based on the solvent vapor treated blend films is lower that that of the devices based on the as cast films. It is widely accepted that the energy difference between the HOMO and LUMO of the acceptor determines the $V_{\rm oc}$ value of the organic BHJ PV devices. We have already shown that the overall optical absorption spectrum of the solvent vapor treated blend films is redshifted. This result can be interpreted assuming that the red-shifted spectrum results from a lower energy state of delocalized exciton in donor materials (M1 or M2), as reported for conjugated polymers [58]. Therefore, the lowering of $V_{\rm oc}$ for devices based on the solvent vapor treated blends can be explained by reduced optical band gap of M1 or M2.

We have investigated the charge collection efficiency by means of the space charge limited current (SCLC) measurements in dark. In the case of the devices based on the as cast blend films, the space charge limits the charge collection efficiency, because the hole mobility is lower than the electron mobility. According to the SCLC criteria, when there is a large difference between the hole and electron mobilities, the half power dependence of the photocurrent on the applied voltage takes place, and the FF can not exceed more than 0.40. Thus, in order to obtain high charge collection efficiency, it is necessary to balance the carrier mobility by enhancing the hole mobility in the blend. To investigate the space charge effects, we extract the hole and electron mobilities from the SCLC *I-V* characteristics obtained in the dark for hole and electron only devices [55a.57]. We have fabricated the hole- and electron-only devices having structure ITO/PEDOT:PSS/M1 or M2:PCBM/Au and ITO/PED-OT:PSS/M1or M2:PCBM/Al, respectively. The hole and electron mobilities have been extracted from the J-V characteristics using the SCLC model [57] and they are listed in Table 4. It can be seen from this table that the hole mobility has been increased about 7-8 times for the devices based on

Hole and electron mobility of M1:PCBM and M2:PCBM blends films evaluated using the SCLC model.

Film	Hole mobility (μ_h) (cm ² /Vs)	Electron mobility (μ_e) (cm ² /Vs)	$\mu_{\rm e}/\mu_{\rm h}$
M1:PCBM (as cast)	$1.2 imes 10^{-6}$	$6.4 imes10^{-5}$	53
M1:PCBM (solvent vapor treated)	$9.7 imes10^{-6}$	$6.5 imes 10^{-5}$	6.9
M1:PCBM (thermally annealed solvent vapor treated)	$1.5 imes 10^{-5}$	$6.9 imes 10^{-5}$	4.6
M2:PCBM (as cast)	$0.96 imes10^{-6}$	$6.8 imes 10^{-5}$	71
M2:PCBM (solvent vapor treated)	$6.8 imes 10^{-6}$	$7.0 imes 10^{-5}$	10.3
M2:PCBM (thermally annealed solvent vapor treated)	$9.6 imes10^{-6}$	$7.0 imes10^{-5}$	7.3

the solvent vapor treated blend. Moreover, the electron mobilities with and without solvent annealing are almost the same. The increase in hole mobility after solvent vapor treatment is attributed to the enhance in the crystallinity and surface roughness of the **M1** or **M2** as indicated from the absorption spectra and AFM images. The mobility difference between the holes and electrons decreases remarkably and reduces the effect of space charge for the devices based on solvent vapor treated blends. Therefore, we assume that the charge collection efficiency has been increased for these devices resulting in improvement in the overall PCE of the devices.

Finally, we have investigated the PV response of the devices based on thermally annealed on the solvent vapor treated blends. The I-V characteristics of these devices are shown in Fig. 11. The PV parameters are summarized in Table 3. Both V_{oc} and J_{sc} have been increased for these devices as compared to devices based on solvent vapor treated blends. The PCE has been further increased up to 3.57% and 2.42% with the thermally annealed solvent treated M1:PCBM and M2:PCBM blend, respectively. This increase in PCE may be attributed to a further increase in the crystallinity of the blend upon the thermal treatment. We have also measured the hole and electron mobility for the devices based on the thermally annealed solvent vapor treated blends and found that the hole mobility has been further increased (as shown in Table 4). Moreover, the electron mobility has also been increased by 20



Fig. 11. Current–voltage characteristics of the devices based on THF treated and thermally annealed **M1**:PCBM and **M2**:PCBM blend under illumination intensity of 100 mW/cm².

times as compared to the solvent treated blend, indicating that thermal annealing can effectively activate PCBM molecules to diffuse and aggregate into clusters for better charge transport. The increase in both electron and hole mobilities for the device based on the thermally annealed solvent vapor treated blends, further reduces the space charge effect, improves the charge transport and charge collection leading to the overall PCE of the device.

4. Conclusions

Two new molecules **M1** and **M2** of low band gap which contained a central spacer and 4-nitro-α-cyanostilbene terminal units were synthesized. They were soluble in common organic solvents. Their long-wavelength absorption maximum was at 590-640 mm with thin film absorption onset at 742 nm corresponding to an optical band gap of 1.67 eV. The electrochemical band gap estimated from the cyclic voltammetery data is 1.70 eV, which is very close to the optical band gap. However, the HOMO and LUMO of M1 and M2 are at different energy levels. We have used both M1 and M2 as electron donor for BHJ PV devices along with PCBM as electron acceptor. The hole mobility of M1 is higher than that of M2. The PCE for pristine M1:PCBM and M2:PCBM is 1.67% and 1.05%, respectively. The higher value of PCE for M1:PCBM is due to the higher hole mobility of this molecule. The devices with solvent vapor treated shows PCE 3.05% and 1.90% for M1:PCBM and M2:PCBM, respectively. The improved PCE has been interpreted in terms of more balanced charge transport due to the modified nanoscale morphology and increased crystallization of the blend. The PCE has been further increased up to 3.57% and 2.42% for the devices based on thermally annealed solvent vapor treated blend M1:PCBM and M2:PCBM, respectively. This has been attributed to the higher balance charge transport due to both increases in electron and hole mobilities in the blend. Our studies indicate that a combination of thermal annealing and solvent vapor treatment is an effective approach to improve the PCE of organic BHJ PV device.

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