Contents lists available at ScienceDirect

Organic Electronics



journal homepage: www.elsevier.com/locate/orgel

Low band-gap phenylenevinylene and fluorenevinylene small molecules containing triphenylamine segments: Synthesis and application in bulk heterojunction solar cells

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ARTICLE INFO

Article history: Received 19 November 2010 Received in revised form 4 January 2011 Accepted 13 February 2011 Available online 26 February 2011

Keywords: Bulk heterojunction solar cells Low band gap Small molecule Solvent effect Triphenylamine Phenylenevinylene Fluorenevinylene

ABSTRACT

Starting from triphenylamine, two low band gap small molecules, PH and FL, based on phenylenevinylene and fluorenevinylene, respectively were synthesized. They were soluble in common organic solvents such as tetrahydrofuran, chloroform and dichloromethane. Their long-wavelength absorption maximum was at 605-643 nm with optical band gap of 1.64-1.66 eV. These small molecules showed a band gap lower than that of P3HT and also have deeper HOMO level, which is beneficial for improvement of the open circuit voltage. The photovoltaic properties have been investigated using the bulk heterojunction (BH]) active layer of PH or FL with PCBM. The device based on FL:PCBM displayed higher power conversion efficiency (PCE) (1.42%) than the device based on PH:PCBM (1.02%), when the blend films were cast from chloroform solvent. Moreover, various casting solvents were used for the BHJ solar cells based on FL:PCBM blend and their effect on the photovoltaic performance was investigated. The results indicate that high boiling point solvents lead to an enhanced self-organization of FL in the active layer, which causes an increased charge transport. Finally, we have used a modified PCBM, i.e. F as electron acceptor along with FL as electron donor, to increase the light harvesting in the wavelength region below 500 nm and the PCE is about 4.38% when the BHJ (FL:F blend) device was spin casted from mixed 1-chloronaphthalene/o-dichlorobenzene solvents. The improved PCE has been attributed to the increased light absorption and higher hole mobility in the active layer, which resulted in more balanced charge transport.

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1566-1199/\$ - see front matter \odot 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.orgel.2011.02.008

Abbreviations: A, acceptor; AFM, atomic force microscopy; BHJ, bulk heterojunction; CB, chlorobenzene; CF, chloroform; CN, 1-chloronaphthalene; CV, cyclic voltammetry; D, donor; DCB, o-dichlorobenzene; DMF, *N*,*N*-Dimethylformamide; E_{g}^{opt} , optical band gap; E_{onset}^{ox} , onset oxidation; E_{onset}^{red} , onset reduction; FF, fill factor; HOMO, highest occupied molecular orbital; ICT, intramolecular charge transfer; IPCE, incident photon to current efficiency; ITO, indium tin oxide; *J*-V, current-voltage; *J_{sc}*, short circuit current; $\lambda_{a,max}$, long-wavelength absorption maximum; LUMO, lowest unoccupied molecular orbital; OPV, organic photovoltaic; OSCs, organic solar cells; P3HT, poly(3-hexylthiophene); PCBM, [6,6]-phenyl-C-61-butyric acid methyl ester; PCE, power conversion efficiency; PV, photovoltaic; ms, root mean square; SCLC, space charge limited current; SM, small-molecule; THF, tetrahydrofuran; TPA, triphenylamine; V_{oc}, open circuit voltage; XRD, X-ray diffraction.

1. Introduction

Organic semiconducting materials open the way of lowcost, flexible, and large-scale solar cells. Recently, power conversion efficiencies (PCEs) above 5% and to 6.1% have been reported for bulk-heterojunction (BHJ) solar cells [1–3]. These solar cells comprising interpenetrating networks of an organic donor (D) and a fullerene derivative acceptor (A) such as [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) constitute a promising technology because they are easy to fabricate by solution processing and are predicted theoretically to yield PCEs of up to 10-15% if a suitable low band gap donor material is discovered [4]. Although considerable research effort has been expended to develop such low band-gap donor materials [5], the highest reported efficiencies have been dominated by conjugated polymers such as poly(3-hexylthiophene) (P3HT) [6–9]. This system has been explored thoroughly for the past decade. The high efficiency of P3HT-fullerene devices can be explained by the ability of the blend to phase separate and crystallize into desirable BHJ morphologies after processing, allowing for efficient charge separation and transport [10,11]. The current effort in this area was focused on developing the low band gap polymers to harvest the near infrared light [12]. However, polymers have problems of poor reproducibility, difficulty in purification, and poor controllability in the molecular weight. Thus efforts have been laid on developing solution processable low band gap organic SM donors, because they offer advantages of easy synthesis and purification and mono-dispersion in the molecular weight, which greatly improve the reproducibility in the performance of the devices.

Most of the researchers related to BHJ solar cells have focused on polymeric donor materials, since they generally have better film-forming properties than non-polymeric materials [13]. Small-molecule (SM) 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 lower relative to solution processed solar cells using polymeric donor materials. SM 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 [14,15]. SMs 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 SMs a promising class of donor material for BHJ solar cell applications [16-24]. The PCE of solution processable SMs has steadily improved up to in the range 2.0-4.4% [25], due to considerable efforts towards the development of new SMs having low band gap and semiconducting property. Particularly, significant progress has been made in the synthesis and processing of donor-acceptor (D-A) SMs. Theoretical and experimental progresses in organic solar cells (OSCs) have demonstrated that such D-A SMs and polymers have great potential to be one class of promising materials for OSCs. D–A SMs can be considered as efficient donor materials for OSCs because of the fact that the absorption spectrum of theses molecules can be extended towards longer wavelengths by intra-molecular charge transfer (ICT) transition between donor and acceptor inside molecules [21] and the energy level can be easily controlled by introducing various electron donating or acceptor groups into the molecules.

On the other hand, a number of polyfluorenes and their derivatives have been studied as a photoactive structure in polymer light-emitting devices and solar cells on account of their large band gap, high photoluminescence, electroluminescence efficiencies, good thermal/chemical stability, and good solubility in common organic solvents. Alternating polyfluorene copolymers with various band gaps have been synthesized, and solar cells based on some of these copolymers have demonstrated PCEs of $\sim 1\%$ [26,27]. A literature survey revealed that certain fluorene containing copolymers have been synthesized and used for BHJ solar cells very recently [28-32]. Finally, among the various types of reported polymer semiconductors, poly(p-phenylenevinylenes) (PPVs) [33-35] and their derivatives are widely used in solar cell applications as p-type donor materials. Poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenlenevinylene] (MEH-PPV) is a PPV derivative which has been mainly used as electron donor for BHJ solar cells [36].

A series of low band gap SMs that contain cyanovinylene 4-nitrophenyl segments have been recently synthesized in our laboratory and used as donors with PCBM as acceptor for BHJ solar cells [37-41]. Additionally, we have very recently synthesized a modified PCBM derivative F (Scheme 1) carrying cyanovinylene 4-nitrophenyl segment [42]. Specifically, PCBM has been hydrolyzed to carboxylic acid and then converted to the corresponding carbonyl chloride. The latter was condensed with 4-nitro-4'-hydroxy- α -cyanostilbene to afford **F**. It showed higher solubility than PCBM in common organic solvents due to the increase of the organic moiety. Both solutions and thin films of F displayed stronger absorption than PCBM in the range of 250-900 nm. BHJ solar cells based on P3HT as electron donor with **F** as electron acceptor exhibited a PCE of 4.23%, while the device based on P3HT:PCBM exhibited PCE of 2.93% under the same conditions [42].

Herein, we report the synthesis of two low band gap SMs, **PH** and **FL**, based on phenylenevinylene and fluorenevinylene, respectively. They contain certain common structural characteristics, namely triphenylamine (TPA) and cyanovinylene 4-nitrophenyl segments. They are only



Scheme 1. Chemical structures of the electron acceptors (PCBM and \mathbf{F}) used in this investigation.

differentiated by their central unit which is 2,5-dihexyloxy(phenylenevinylene) for PH and 9,9-dihexyl(fluorenevinylene) for FL. The aliphatic chains which are attached to the central unit enhanced the solubility of these SMs. They were successfully synthesized by a four-step reaction sequence. The last step of their synthesis included the condensation of a key-tetraaldehyde with 4-nitrobenzyl cyanide. Both SMs possess the D-A architecture. Specifically, they carry phenylenevinylene/fluorenevinylene and TPA as D units and cyanovinylene 4-nitrophenyl as A units which allow an intramolecular charge transfer (ICT), thus reducing the optical band gap (E_g^{opt}) of the SMs. Moreover, the presence of the TPA moieties is expected to increase the hole mobility of both SMs. We have used these SMs as electron donor along with PCBM or modified PCBM, i.e. F as electron acceptor for the fabrication of BHJ PV devices. The PCEs for the devices based on PH:PCBM and FL:PCBM cast from chloroform solvent are 1.02% and 1.46%, respectively. In addition, we investigated the effect of solvent used for the spin casting of the FL:PCBM blend on the PV response of the device and found that the solvent has a strong influence on the morphology of the blend films and on the PCE of the device. Finally, we have replaced the electron acceptor PCBM by the modified PCBM, i.e. F, which has strong absorption at lower wavelength region (below 500 nm) and fabricated BHJ devices using FL as electron donor. We have achieved PCE about 3.62% and 4.38% for FL:F BHJ active layer cast from o-dichlorobenzene (DCB) and 1-chloronaphthalene/ o-dichlorobenzene (CN/DCB) solvent, respectively. The BHJ cast from the mixed solvents (CN/DCB) leads to an enhanced self organization and crystallinity of FL in active layer, which causes an increased charge transport, incident absorption and higher carrier mobility in the active layer thus contributing to the enhancement in the device performance.

2. Experimental

2.1. Reagents and solvents

4-Nitrobenzyl cyanide was synthesized from the nitration of benzyl cyanide with concentrated nitric and sulfuric acid [43]. It was recrystallized from ethanol. 1,4-Divinyl-2,5-bis(hexyloxy)-benzene was prepared by Stille coupling reaction [44] of 1,4-dibromo-2,5-bis(hexyloxy)-benzene with tributylvinyltin [45]. 9,9-Dihexyl-2,7-divinylfluorene was prepared by Stille coupling [44] of 2,7-dibromo-9,9-dihexylfluorene with tributylvinyltin [46]. *N*,*N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were dried by distillation over CaH₂. Triethylamine was purified by distillation over KOH. All other reagents and solvents were commercially purchased and were used as supplied.

2.2. Preparation of small molecules

2.2.1. Compound 3a

A flask was charged with a mixture of **2** (0.2957 g, 0.778 mmol), 1,4-divinyl-2,5-bis(hexyloxy)-benzene (0.1285 g,

0.389 mmol), $Pd(OAc)_2$ (0.0017 g, 0.007 mmol), $P(o-tolyl)_3$ (0.0047 g, 0.015 mmol), DMF (10 mL), and triethylamine (3 mL). The flask was degassed and purged with N₂. The mixture was heated at 90 °C for 24 h under N₂. Then, it was filtered and the filtrate was poured into methanol. The precipitate was filtered and washed with methanol. The crude product was purified by dissolving in THF and precipitating into methanol (0.3072 g, yield 85%).

FT-IR (KBr, cm⁻¹): 2952, 2926 (C–H stretching of hexyloxy chains); 1676 (formyl); 3030, 1590, 1506 (aromatic); 1320 (C–N stretching of triphenylamine); 1286, 1272, 1214 (ether bond); 967 (*trans* vinylene bond).

¹H NMR (CDCl₃) ppm: 9.80 (s, 4H, formyl); 7.67 (m, 8H, TPA ortho to formyl); 7.30–7.2 (m, 16H, other TPA; 4H, vinylene); 6.75 (s, 2H, phenylene); 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 $C_{62}H_{60}N_2O_6$: C, 80.14; H, 6.51; N, 3.01. Found: C, 79.92; H, 6.43; N, 3.17.

2.2.2. Compound 3b

Compound **3b** was similarly prepared in 80% yield (0.22 g) from the reaction of **2** (0.2106 g, 0.554 mmol), with 9,9-dihexyl-2,7-divinylfluorene (0.1071 g, 0.277 mmol) in DMF (10 mL) in the presence of triethylamine (3 mL), Pd(OAc)₂ (0.0012 g, 0.005 mmol) and P(o-tolyl)₃ (0.0034 g, 0.011 mmol).

FT-IR (KBr, cm⁻¹): 2950, 2925 (C–H stretching of hexyl chains); 1675 (formyl); 3029, 1592, 1504 (aromatic); 1315 (C–N stretching of TPA); 965 (*trans* vinylene bond).

¹H NMR (CDCl₃) ppm: 9.80 (s, 4H, formyl); 7.72 (m, 2H, H4 of fluorene); 7.67–7.60 (m, 4H, H1 and H3 of fluorene; 8H, TPA ortho to formyl); 7.30–7.02 (m, 16H, other TPA; 4H, vinylene); 2.06 (m, 4H, $CH_2(CH_2)_4CH_3$); 1.11 (m, 16H, $CH_2(CH_2)_4CH_3$); 0.78 (t, 6H, $(CH_2)_5CH_3$).

Anal. Calcd. for $C_{69}H_{64}N_2O_4$: C, 84.11; H, 6.55; N, 2.84. Found: C, 83.85; H, 6.64; N, 2.68.

2.3. Small molecule PH

A flask was charged with a solution of **3a** (0.3614 g, 0.389 mmol) and 4-nitrobenzyl cyanide (0.2523 g, 1.556 mmol) in DMF (15 mL). Sodium hydroxide (0.20 g, 5.00 mmol) dissolved in ethanol (5 mL) was added portionwise to the stirred solution. The mixture was stirred for 1 h at room temperature under N₂ and then was concentrated under reduced pressure. Water was added to the concentrate and the product precipitated as a dark green solid. It was filtered, washed thoroughly with water and dried to afford **PH**. It was purified by column chromatography, eluting with a mixture of dichloromethane and hexane (1:1) (0.46 g, 80%).

FT-IR (KBr, cm⁻¹): 2950, 2924 (C–H stretching of hexyloxy chains); 2158 (cyano); 1524, 1344 (nitro); 1316 (C–N stretching of TPA); 1284, 1248 (ether bond); 1584, 1504 (aromatic); 965 (*trans* vinylene bond); 1013 (cyanovinylene).

¹H NMR (CDCl₃) ppm: 8.19 (m, 8H, phenylene ortho to nitro); 7.83 (s, 4H, cyanovinylene); 7.52 (m, 8H, phenylene meta to nitro); 7.30–7.13 (m, 24H, TPA); 7.10 (m, 4H, vinylene); 6.75 (s, 2H, phenylene ortho to oxygen); 3.96 (m, 4H,

 $\begin{array}{l} {\rm OCH}_2({\rm CH}_2)_4{\rm CH}_3); \ 1.81 \ (m, \ 4H, \ {\rm OCH}_2{\rm CH}_2({\rm CH}_2)_3{\rm CH}_3); \ 1.37 \\ (m, \ 12H, \ {\rm O(CH}_2)_2({\rm CH}_2)_3{\rm CH}_3); \ 0.91 \ (t, \ 6H, \ {\rm O(CH}_2)_5{\rm CH}_3). \\ {\rm Anal. \ Calcd. \ for \ C_{94}H_{76}N_{10}O_6: \ C, \ 74.98; \ H, \ 5.09; \ N, \ 9.30. \end{array}$

Found: C, 74.37; H, 4.82; N, 9.13.

2.4. Small molecule FL

FL was similarly prepared in 83% yield (0.36 g) from the reaction of **3b** (0.2729 g, 0.277 mmol) with 4-nitrobenzyl cyanide (0.1797 g, 1.108 mmol) in DMF (15 mL) in the presence of sodium hydroxide (0.20 g, 5.00 mmol).

FT-IR (KBr, cm⁻¹): 2950, 2924 (C–H stretching of hexyl chains); 2160 (cyano); 1522, 1346 (nitro); 1314 (C–N stretching of TPA); 1584, 1506 (aromatic); 964 (*trans* vinyl-ene bond); 1004 (cyanovinylene).

¹H NMR (CDCl₃) ppm: 8.19 (m, 8H, phenylene ortho to nitro); 7.83 (s, 4H, cyanovinylene); 7.72 (m, 2H, H4 of fluorene); 7.60 (m, 4H, H1 and H3 of fluorene); 7.52 (m, 8H, phenylene meta to nitro); 7.30–7.13 (m, 24H, TPA); 7.10 (m, 4H, vinylene); 2.06 (m, 4H, $CH_2(CH_2)_4CH_3$); 1.11 (m, 16H, $CH_2(CH_2)_4CH_3$); 0.78 (t, 6H, $(CH_2)_5CH_3$).

Anal. Calcd. for $C_{101}H_{80}N_{10}O_8$: C, 77.67; H, 5.16; N, 8.97. Found: C, 77.38; H, 5.21; N, 9.20.

2.5. 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 tetramethylsilane as an internal standard. UV–Vis spectra were recorded on a Beckman DU-640 spectrometer. Elemental analyses were carried out with a Carlo Erba model EA1108 analyzer.

The electrochemical properties of both SMs, i.e. **PH** and **FL** were examined using cyclic voltammetry (CV) (EDCA electrochemistry system). A glassy carbon electrode was used as working electrode. The SMs were coated on glassy carbon electrode from tetrahydrofuran (THF) solution and immersed in 0.1 mol/L Bu₄NPF₆ acetonitrile solution used as supporting electrolyte. Cyclic voltammograms were recorded, using Ag/Ag+ as reference electrode at a scan rate of 100 mV/s.

The crystallinity of the films was studied using the X-ray diffraction (XRD) technique (panalytical make USA) having CuK α , as radiation source of wavelength λ = 1.5405 Å with the films coated on the quartz substrates. Atomic force microscopy (AFM) images were recorded using digital instrument nanoscope in trapping mode.

2.6. Device fabrication and characterization

All the devices were fabricated on indium tin oxide (ITO) coated glass substrates. The ITO coated glass substrates were cleaned with acetone in an ultrasonic bath. A thin layer of poly(3,4-ethylene-dioxythiophene): poly(styrene sulfonate) (PEDOT:PSS) (70 nm) was spin coated on it from PEDOT:PSS aqueous solution at 2000 rpm and dried subsequently at 80 °C for 20 min in air, and then transferred into a glove box. The active layer of the blend of **PH** or **FL** with PCBM was spin coated from different solvents (chloroform,

chlorobenzene, o-dichlorobenzene, and 2% additive 1-chloronaphthalene (CN) in o-dichlorobenzene), onto the PED-OT:PSS layer, and then dried in ambient conditions. The concentration of **PH** or **FL**:PCBM blend solution used in this study for spin coating was 10 mg/mL in the solvent used. The thickness of the active layers is approximately 90–95 nm. The structure of the device is ITO/PEDOT:PSS/**PH** or **FL**:PCBM/AI. The effective active area of the devices is about 20 mm². Current–voltage (*J*–*V*) characteristics of the devices were measured using a computer controlled Keithley 238 source meter in dark and under illumination intensity of 100 mW/cm² in ambient conditions. A xenon light source was used to give simulated irradiance of 100 mW/cm² (equivalent to and AM1.5 irradiation) at the surface of the device.

We have also fabricated BHJ devices based on **FL:F** using the same method. To measure the hole and electron mobilities, the devices having structure ITO/PEDOT:PSS/**FL:F**/Au and Al/**FL:F**/Al were used, respectively and the *J*-*V* characteristics in dark have been recorded.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 2 outlines the four-step reaction for the synthesis of SMs. Compounds **1** [47] and **2** [48] have been synthesized according to reported methods. Compound **2** reacted with 1,4-divinyl-2,5-bis(hexyloxy)-benzene and 9,9-dihexyl-2,7-divinylfluorene in a mol ratio 2:1 to afford **3a** and **3b**, respectively. This reaction took place in DMF using Et₃N as acid scavenger and Pd(OAc)₂ as catalyst. Finally, the condensation of **3a** and **3b** with 4-nitrobenzyl cyanide in the presence of sodium hydroxide gave **PH** and **FL**, respectively. These SMs were soluble in common organic solvents such as tetrahydrofuran, chloroform and dichloromethane owing to the aliphatic chains.

The SMs were characterized by FT-IR and ¹H NMR spectroscopy. The IR spectra showed common absorption bands approximately at 2952, 2926 (C–H stretching of aliphatic chains); 2128 (cyano); 1524, 1344 (nitro); 1316 (C–N stretching of TPA); 1584, 1504 (aromatic); 965 (vinylene), and 1013 cm⁻¹ (cyanovinylene). On the other hand, the ¹H NMR spectra of SMs displayed common signals at 8.19 (phenylene ortho to nitro); 7.83 (cyanovinylene); 7.52 (phenylene meta to nitro); 7.30–7.13 (TPA) and 7.10 ppm (vinylene). Finally, the aliphatic chains resonated at the range of 3.96–0.91 ppm for **PH** and 2.06–0.78 ppm for **FL**.

3.2. Photophysical and electrochemical properties

Fig. 1 depicts the UV–Vis absorption spectra of SMs in both dilute (10^{-5} M) THF solution and thin film. All photophysical and electrochemical characteristics of SMs are summarized in Table 1. The solutions showed long-wavelength absorption maximum ($\lambda_{a,max}$) or shoulder around 605 and 643 nm, while the thin films showed $\lambda_{a,max}$ at 626–632 nm. The spectra were broad and extended approximately up to 750 nm in solutions and 800 nm in



Scheme 2. Synthesis of SMs PH and FL.

thin films which is desirable for PV applications. This feature was attributed to an ICT between the electrondonating central unit (phenylenevinylene/fluorenevinylene and TPA) and the electron-accepting terminal units (cyanovinylene 4-nitrophenyl). The thin film absorption onset was located at 758 and 746 nm corresponding to an E_g^{opt} of 1.64 and 1.66 eV for **PH** and **FL**, respectively. The optical properties of SMs are similar thus supporting that their central unit did not influence significantly their photophysical characteristics.

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the organic polymers and SMs are important parameters in the design of organic photovoltaic (OPV) devices, and they can be estimated from the onset oxidation (E_{onset}^{ved}) and reduction (E_{onset}^{red}) potentials [49]. Fig. 2 shows the cyclic voltammograms of **PH** and **FL**. Similar cyclic voltammograms have been reported for other small molecules in the literature [50]. The E_{onset}^{ox} and E_{onset}^{red} potentials vs. Ag/Ag+ (Table 1) were used for calculation of the HOMO and LUMO energy levels according to the following expressions [51].

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

The values of the HOMO and LUMO levels of the **PH** and **FL** are given in Table 1. The LUMO level of both SMs is the same but the HOMO level is -5.35 and -5.30 eV for **PH** and

FL, respectively. This implies that the HOMO levels are mainly affected by the D unit in SM, while the LUMO levels (-3.55 eV) are primarily controlled by the acceptor moieties. Since the LUMO level of PCBM is -3.95 eV, the energy difference between the LUMOs of these SMs and PCBM is about 0.3-0.4 eV, which should be sufficient for the exciton splitting and charge dissociation [52]. In addition, the deeper HOMO level of these SMs is desirable for higher open circuit voltage (V_{oc}) of the OPVs with organic semiconductors as D materials because the V_{oc} is usually proportional to the difference between the LUMO level of the acceptor and the HOMO level of the D. The electrochemical band gaps have been estimated from the energy difference between the HOMO and LUMO levels and they are 1.80 and 1.75 eV for **PH** and **FL**, respectively.

3.3. Photovoltaic properties

Fig. 3(a) shows the *J*–*V* characteristics of the OPVs based on SMs (**PH** or **FL**):PCBM cast from the chloroform solvent. The PV parameters of the OPVs, including V_{oc} , short circuit current (J_{sc}), fill factor (FF) and power conversion efficiency (PCE) are summarized in Table 2. The higher value of V_{oc} for the device based on **PH**:PCBM is attributed to the lower HOMO level of **PH** as compared to **FL**. The OPV based on the **FL**:PCBM blend showed higher J_{sc} and FF than the **PH**:PCBM based device, leading to PCE of 1.46% vs. 1.02%, respectively. However, the current density is still much





Fig. 2. Cyclic voltammograms of (a) PH and (b) FL.

Fig. 1. UV–Vis absorption spectra of SMs in THF solution (top) and thin film (bottom).

lower than that for the state-of-the-art polymer/fullerene systems [13]. In order to understand the origins of the low current, we carried out the incident photon to current efficiency (IPCE) measurements. The IPCE spectra of the PV devices, as shown in Fig. 3(b), are consistent with the absorption spectra of the blend films of the active layers. The absorptions at shorter wavelength region, below 420 nm, are mainly contributed to PCBM, while those at longer wavelength region are contributed to SMs. The higher J_{sc} of the **FL**:PCBM based device compared to the **PH**:PCBM device is reflected on the higher IPCE values in the wavelength region corresponding to absorption of SMs. The higher value of the J_{sc} and PCE may also be

attributed to the higher value of hole mobility for the device based on the **FL** film.

The relatively lower PCE of SM BHJ OSCs becomes the biggest hindrance to commercial application. In the case of OSCs based on polymers, some approaches have been used to improve the device efficiency including thermal annealing or utilizing additive to control the formation of interpenetrating D/A networks at nanometer scale for efficient exciton dissociation and charge transport within the BHJ devices [53]. The solvents used for the preparation of the active layer have shown a strong impact on the morphology of the blend films, which influence the performance of the devices. However, these methods are

Table 1			
Optical and	electrochemical	properties	of SMs.

SM	$\lambda_{a,max}^{a}$ in solution (nm)	$\lambda_{a,max}^{a}$ in thin film (nm)	Thin film absorption onset (nm)	E ^{opt b} (eV)	E ^{ox} onset (V)	E ^{red} onset (V)	HOMO (eV)	LUMO (eV)	E ^{el c} (eV)
PH	(604) 643	632	758	1.64	0.65	-1.15	$-5.35 \\ -5.30$	-3.55	1.80
FL	605 (648)	626	746	1.66	0.60	-1.15		-3.55	1.75

Numbers in parentheses indicate a shoulder in the UV-Vis spectrum.

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

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

 $c E_{g}^{q}$: Electrochemical band gap determined from cyclic voltammetry.



Fig. 3. (a) Current–voltage (J-V) characteristics and (b) IPCE spectra of the OSCs based on **PH**:PCBM and **FL**:PCBM cast from CF solvent under illumination of 100 mW/cm².

Table 2 Photovoltaic parameters of the devices based on PH:PCBM and FL:PCBM cast from chloroform (CF).

Blend	Short circuit current (J _{sc}) (mA/cm ²)	Open circuit voltage (V _{oc}) (V)	Fill factor (FF)	Power conversion efficiency (PCE) (%)
PH:PCBM FL:PCBM	3.7 4.3	0.78 0.74	0.41 0.46	1.02 1.46

generally not applied for SM BHJ solar cells. We have studied the effect of different solvents on the performance of OPVs using the **FL**:PCBM blend.

Fig. 4 shows the UV–Vis absorption spectra of **FL**:PCBM thin films for different casting solvents. By changing the casting solvent certain differentiations appeared in the absorption spectra. For chloroform (CF) cast film the absorption spectra show two absorption bands around 360 and 626 nm. The absorption band having peak around 360 nm stems from PCBM [54], while the absorption band with peak around 626 nm represents the contribution from **FL**. For chlorobenzene (CB) cast film the peak absorption



Fig. 4. Absorption spectra of **FL**:PCBM films (1:1 w:w) prepared by spin casting from different solvents.

wavelength is at 635 nm showing a 10 nm red-shift, with one shoulder peak around 670 nm. Compared to the former two films absorption spectra cast from CF and CB, the absorption spectrum of o-dichlorobenzene (DCB) cast film becomes more distinguishable and much stronger. The vibronic absorption is much more pronounced indicating strong interchain–interlayer interaction in **FL**, as well as a good ordering of blends films. Both significant red shift and pronounced shoulder appear in a more ordered film as high crystallinity order involves an enhanced conjugation length and hence a shift of the absorption spectra to lower energies.

Fig. 5 shows the XRD results from active layer FL:PCBM prepared by spin coating from various solvents. The XRD intensities values were obtained from peaks at $2\theta = 8.26^{\circ}$ are 6.3, 10.5, 14.8, and 19.4 for the films cast from CF, CB, DCB, and CN/DCB solvents, respectively. These values correspond to the interchain spacing in FL associated with the degree of crystallinity. When high boiling point solvents (DCB and CB) instead of low boiling point (CF) were used for the active layer, the increased intensities were observed in the peak at $2\theta = 8.26^{\circ}$. This indicates the active layers prepared from DCB and CB have higher ordered structure and more improved crystallinity than CF. In the high boiling point solvents, **FL** in the active layer may have longer time to solidify due to the slow evaporation rate of the solvents and the slow film growth rate may assist to form the high degree of self organized structure. The crystalline nature of the blend has been further improved as can be seen for the XRD pattern.



Fig. 5. X-ray diffraction spectra for **FL**:PCBM (1:1 w/w) blend thin films prepared from different solvents.



Fig. 6. Current–voltage (J-V) characteristics of the OSCs for **FL**:PCBM cast from different solvents under illumination intensity of 100 mW/cm².

Table 3 Summary of the photovoltaic parameters of the ITO/PEDOT:PSS/FL:PCBM/ Al devices prepared from different solvents.

Solvent type	J _{sc} (mA/cm ²)	$V_{\rm oc}\left({ m V} ight)$	FF	PCE (%)
CF	4.3	0.74	0.46	1.46
CB	5.1	0.74	0.48	1.81
DCB	6.0	0.76	0.53	2.42
CN/DCB	/.15	0.76	0.57	3.0

The *I–V* characteristics under illumination intensity AM 1.5 (100 mW/cm^2) for the OSCs fabricated from various solvents employing FL:PCBM blend are shown in Fig. 6. The PV parameters of the devices are summarized in Table 3. It is seen from this table that the $V_{\rm oc}$ does not change under various solvent conditions but the J_{sc} and FF show a differentiation. Compared to the device made from CF solvent, the device based on CB solvent leads to an increase of PCE from 1.42% to 1.81%. Moreover, a PCE of 2.42% is observed from the device fabricated from DCB solvent. and the device fabricated from mixed CN/DCB solvents possesses PCE of 3.0%. The improvement of PCE for the devices is mainly due to the enhancement in both I_{sc} and FF values. This indicates an improved charge transport due to the expansion of the crystalline domains. The reason for this improved crystallinity in the coated films can be the different solvent evaporation speed during spin coating, since CF has a low boiling point of 60 °C, while the boiling points of CB and DCB are 130 and 180 °C, respectively. The film cast from DCB solvent is frozen very slowly owing to the high boiling point of DCB. This slow freezing of FL may cause a longer time for the FL self organization, leading to a higher degree of ordering in the material. The broadening of the absorption band and red shift in the absorption peak leads to an increase of the light harvesting by the active layer. The higher PCE for the device fabricated from mixed solvents (CN/DCB) is attributed to the increased ordering of the blend, which provides a more increased D-A interfacial area. The combined effects of the above leads to an increase in the overall PCE of the device.

3.4. Photovoltaic properties with F as electron acceptor

For the acceptor materials in OSCs, PCBM offers the advantage of good solubility in organic solvents, high electron mobility and high electron affinity. However, weak absorption in the visible region and a low LUMO energy level are the weak points of PCBM. Weak absorption in the visible region limits its contribution to light harvesting in the PV conversion. We attempted to increase the breadth of the IPCE spectrum and the overall PCE, by fabricating OSCs with a more light absorbing modified PCBM, i.e. F [42]. Fig. 7(a) shows the J-V curves of the devices based on FL:F (1:1 w/w) spin coated from DCB and CN/DCB solvents. The V_{oc} , J_{sc} , FF, and PCE of the devices are listed in Table 4. The devices based on F as electron acceptor show higher value of $V_{\rm oc}$ as compared to that for PCBM. This is attributed to the difference between the LUMO energy levels in PCBM (-3.95 eV) and F (-3.75 eV) [42], because the value of V_{oc} in BHJ photovoltaic device is related to the difference between the HOMO level of the donor and the LUMO level of the acceptor. The device fabricated with FL:F blend shows higher PCE (3.62%) as compared to FL:PCBM (2.42%) based device, cast from DCB. The overall PCE of the device based on FL:F has been further improved up to 4.38% when the blend is cast from



Fig. 7. (a) Current–voltage (*J*–*V*) characteristics and (b) of the OSCs for **FL:F** based on **FL:**PCBM cast from DCB and CN/DCB solvents.

Table 4

Summary of the photovoltaic parameters of the ITO/PEDOT:PSS/**FL:F**/Al devices prepared from different solvents.

Solvent	$J_{\rm sc}~({\rm mA/cm^2})$	$V_{\rm oc}\left({\rm V} ight)$	FF	PCE (%)
DCB	7.4	0.90	0.56	3.62
CN/DCB	8.3	0.88	0.60	4.38

mixed CN/DCB solvents. Fig. 7(b) shows the IPCE spectra of the devices fabricated from blends of **FL:F** cast from OCB and CN/DCB solvents. The IPCE spectra are similar with the absorption spectra of the blend. With the addition of CN in the solvent, the IPCE maximum at 630–680 nm increased from 55% to 71%, which is consistent with J_{sc} and PCE. The J_{sc} value calculated from the integration of the IPCE spectrum is 7.1 and 8.6 mA/cm² for the devices based on DCB and CN/DCB cast blends, respectively, which closely matches the J_{sc} values obtained from the J-V measurements under white light illumination.

The increase of J_{sc} is mainly related to more exciton and charge generation and more effective charge transport. It was found that the film cast from CN/DCB exhibits stronger absorption than that cast from DCB. The stronger absorption partially contributed to higher J_{sc} and IPCE of the device cast from CN/DCB as compared to the device cast from CB. A similar phenomenon has been observed by Yang et al. for P3HT:PCBM system [55].

Another important factor being responsible for increased J_{sc} is the charge transport in active layers. The



Fig. 8. Current–voltage characteristics for (a) hole only and (b) electron only devices based on FL:F blend films with DCB and CN/DCB solvents.

space charge limited current (SCLC) method [56] was adopted to determine the electron and hole mobilities in blend films. Fig. 8(a) shows the dark *I–V* characteristics of the hole only devices having structure of ITO/PEDOT:PSS/ FL:F/Au with the DCB and CN/DCB solvents casting layer films. In order to suppress the electron injection into the blend, a high work function metal gold (Au) was used as cathode. The applied voltage was corrected for the builtin voltage $(V_{\rm bi})$. Compared to the device based on DCB solvent cast film, the device with CN/OCB solvent cast film shows an enhanced current density at the same driving voltage in Fig. 8(a). This indicates that the hole mobility is enhanced due to the self organization of FL. The I-V characteristics for the electron only devices with structure of Al/FL:F/Al are shown in Fig. 8(b). In order to suppress the hole injection into the blend, a low work function metal (Al) was used as anode. The electron and hole mobilities have been measured by fitting the dark *I–V* characteristics for electron and hole only devices, respectively to SCLC model at low voltages, in which the current density is given by

$$J = (9\varepsilon_{\rm o}\varepsilon_{\rm r}\mu V^2/8d^3) \exp[0.891\gamma (V/d)^{0.5}]$$



Fig. 9. AFM images of FL:F blends cast from (a) DCB and (b) CN/DCB solvents (scale 3 \times 3 $\mu m).$

where $\varepsilon_o \varepsilon_r$ represent the permittivity of the material, μ is the mobility, γ is the field activation factor, and d is the thickness of the active layer and voltage $V = V_{appl} - V_{bi}$. The hole (μ_h) and electron (μ_e) mobilities of the film cast from DCB are 5.6×10^{-6} and 3.4×10^{-4} cm²/Vs, respectively. The μ_h and μ_e for the film cast from the CN/DCB are about 1.8×10^{-5} and 2.2×10^{-4} cm²/Vs, respectively. The smaller value of μ_e/μ_h (60.7 and 12.2 for CB and CN/ DCB solvent cast film, respectively) indicates a more balanced charge transport. The more balanced charge transport contributes to the higher J_{sc} and higher PCE.

The difference in PV performance for the devices cast from DCB and CN/DCB solvents is most likely due to the change in the morphology. The effect of the solvents on the active layer morphology was also examined by the AFM technique. Fig. 9 compares the AFM images of the blend films of FL:F cast from the DCB and CN/DCB solvents. For the **FL:F** blend films cast from DCB solvent, its root mean square (rms) roughness is about 0.45 nm. However, when the film is cast from the CN/DCB solvent, the rms roughness is about 0.78 nm. Higher roughness of the film will give higher device efficiency. The rough surface is probably a signature of self organization of organic semiconductor, which in turn enhances ordered structure formation in thin films and increases the carrier mobility [57]. The increased roughness of the active layer enhances the D-A interfacial area leading to efficient dissociation of the excitons into free charge carriers.

4. Conclusions

Two soluble and low band gap SMs, PH and FL, were synthesized. They contained the D-A structure permitting an ICT. The absorption spectra were broad with long-wavelength absorption maximum at 605-643 nm and optical band gap of 1.64-1.66 eV, which is lower than that of P3HT. The HOMO and LUMO levels of both SMs estimated from cyclic voltammetry, suggest that they can be used as donor materials for organic BHJ PV devices. The solution processed organic BHJ PV devices using PH:PCBM and FL:PCBM cast from chloroform solvent show PCE about 1.02% and 1.42%, respectively. We have fabricated BHJ organic PV devices based on the FL:PCBM using various solvents such as chloroform, chlorobenzene, o-dichlorobenzene and mixed CN/DCB and investigated the influence of these solvents on the performance of the solar cells. The device with mixed CN/DCB solvents shows improved performance of PCE of 3.0%. The improved PCE is mainly attributed to the increased value of J_{sc} , which is due to the enhancement in the crystalline nature of the blend.

We have also fabricated BHJ PV devices based on **FL:F** blend to improve the light harvesting efficiency in the lower wavelength region and achieved PCE of about 3.62% and 4.38% with DCB and CN/DCB cast blend, respectively. The improved PCE of the device with **F** as electron acceptor is mainly attributed to both increase in J_{sc} and V_{oc} . The further improvement in the PCE, when the blend is cast from mixed CN/DCB, could be ascribed to efficient exciton dissociation at the D–A interface and a better morphological structure of the active layer.

Acknowledgment

We are thankful to Prof. Y.K. Vijay of Thin film and Membrane Science Laboratory, University of Rajasthan Jaipur (Raj.) for allowing us to undertake the device fabrication and characterization in his laboratory.

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