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Solution processed bulk heterojunction based on A-D-A small molecules with dihydroindoloindole (DINI) central donor with different acceptor end groups

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Four acceptor –donor –acceptor (A-D-A) small molecules with dihydroindoloindole (DINI) as central donor unit and different acceptor end groups such as dicyanovinylene (DCV), indenedione (IND), cyanoacrylate (CA) and rhodanine (Rho) linked through bi-thiophene as π -linkers, DINI-DCV, DINI-IND, DINI-CA and DINI-Rho were designed and synthesized for the application as donor material along with PC₇₁BM as acceptor for solution processed organic bulk heterojunction solar cells. The effect of acceptor end groups on the photovoltaic performance was investigated. The organic solar cells (OSCs) based on as cast **DINI-IND** showed the highest power conversion efficiency of 3.04 % and as cast **DINI-CA** showed the lowest PCE of 1.63 % and other two exhibits the PCE in between them. These results showed that acceptor end group affects the overall performance of the cells. The PCE of OSCs has been further improved up to 7.04 % and 6.16 % employing two step annealing (TSA) treated **DIN-IND**:PC₇₁BM (1:2) and **DIN-CN**:PC₇₁BM (1:2), respectively. The enhancement in the PCE of OSCs with TSA treated active layers is attributed to the better nanophase morphology, the increase in crystalline nature, and light harvesting efficiency and more balanced charge transport and charge collection probability.

Key words: A-D-A small molecules; different end groups; bulk heterojunction solar cells; power conversion efficiency; two step annealing.

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Introduction

Organic solar cells (OSCs) based on the bulk heterojunction (BHJ) active layer are attracting a lot of attention to both academic and industrial communities due to their cost effective and flexible solar energy conversion to electrical energy devices [1]. Significant progress have been made in recent years and power conversion efficiencies (PCEs) over 9-10 % using a single layer polymer BHJ solar cells have been reported [2] after the optimization of donor -acceptor ratio, choice of solvent, solvent and thermal annealing and interface engineering. In contrast to conjugated polymers, conjugated small molecules possess advantages such as simple synthesis, purification, defined molecular structure and molecular weight without batch to batch variation [3]. After the optimization of molecular structure and morphology of BHJ active layer, the PCE of the OSCs has been improved from 0.03% to 9-10% [4]. The π -conjugated small molecules built up from alternating electron-rich donor (D) and electron-poor acceptor (A) segments provide excellent materials with strong charge transfer character, absorptions in the visible to near-infrared region, highest occupied molecular orbital (HOMO) – lowest unoccupied molecular orbital (LUMO) energy gap, and good charge carrier mobility [5]. Among them, acceptor-donor-acceptor (A-D-A) conjugated small molecules were developed and used as donors for solution processed organic solar cells [6]. The electronic levels and solubility of these small molecules can be controlled by proper substitution and functionalization which not only leads to broad absorption of solar spectrum, but also high open circuit voltage and excellent stability towards oxidation.

In the design of new small molecules as electron donor for OSCs, basic properties such as energy levels, charge transport, and absorption are the basic parameters to be considered. Aromatic fused rings have been extensively used to design the high mobility organic semiconductors because the extended conjugation in fused rings is beneficial to form effective interchain π - π overlaps and enhance the charge transport [7], leading to the high charge carrier mobility [8]. Moreover, the extended π -conjugation also results in enhancing the delocalization of π -electrons to attain effective π -conjugation length, reducing to the bandgap [9].

Dihydroindoloindole (DINI) is an electron rich planar aromatic fused structure with two nitrogen atoms, which can be easily substituted with alkyl chains for better solubility of the small material. Owczarczyk et al. reported DINI based polymers and showed that the DINI is an effective backbone for polymer solar cells (PSCs) applications [10]. Kranthiraja et al have also reported the fabrication of BHJ PSCs employing DINI based D-A copolymer,

achieving the PCE of 1.68% [11]. Although DINI has interesting characteristics, the exploration of small molecules based on DINI has not been employed for small molecule BHJ solar cells. We have synthesized a series of A-D-A small molecules with same dihydroindoloindole (DINI) as central donor unit and different acceptor end groups such as dicyanovinylene (DCV), indenedione (IND), cyanoacrylate (CA) and rhodanine (Rho) linked through bi-thiophene linker and investigated their optical and electrochemical properties. We have used these small molecules as donor layer along with PC71BM as acceptor and varied the weight ratio of donor to acceptor and found that 1:2 weight ratio showed best photovoltaic performance. The OSCs fabricated with optimized DINI-CA:PC71BM, DINI-DCV:PC71BM, DINI-Rho:PC71BM and DINI-IND:PC71BM spin cast from DCB showed the PCE of 1.63 %, 2.53 %, 2.13 % and 3.04 %, respectively. Therefore, different acceptor end groups of these small molecules lead to variation in the PCE of OSCs. In order to improve PCE further, we have employed a simple TSA (combined thermal annealing and subsequent solvent vapor annealing) treatment of active layer method and the PCE has been improved significantly (7.04 % and 6.16 % for **DINI-IND**:PC₇₁BM and DINI- $DCV:PC_{71}BM$, respectively) due to the better nanophase morphology, crystallinity, molecular packing and light harvesting ability of active layers. These combined properties enhance the exciton generation efficiency and relatively better balanced charge transport, leading to improvement in J_{sc}, FF and PCE of resulted OSCs.

Experimental details

The synthesis of core and ligands employed for the synthesis of small molecules were described in supplementary information.

2,2'-(5',5''-(5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-diyl)bis(3,4'-dihexyl-2,2'bithiophene-5',5-diyl))bis(methan-1-yl-1-ylidene)dimalononitrile(DINI-DCV):

Malononitrile (120 mmol) dissolved in CHCl₃ (40 mL) was added to **5a** (20 mmol) followed by 2 drops of piperidine. The reaction was stirred for 2 h at room temperature. The mixture was poured into water and extracted with dichloromethane. The organic layer was then dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel (ethylacetate : hexane = 1:5). The crude product was washed with MeOH to afford a purple solid in 65% yield. ¹H NMR (300 MHz, CD₂Cl₂) : δ 7.87 (d, J = 8.4Hz, 1H), 7.73 (s, 1H), 7.57 (s, 1H), 7.53 (s, 1H), 7.33(s, 1H), 7.29 (dd, J = 8.4Hz, 1H), 4.53 - 4.57 (t, 2H), 2.88 - 2.94 (t, 2H), 2.79 - 2.84 (t, 2H), 2.03 - 2.05 (t, 2H), 1.72-1.77(t, 4H), 1.28 - 1.48 (m, 18H), 0.86 - 0.93 (m, 9H). ¹³C NMR (75 MHz, CDCl₃) : δ 150.20, 145.08, 143.73, 142.14, 142.01, 140.97, 140.47, 139.75, 131.92, 131.36, 127.25, 127.07,

119.97, 114.71, 114.08, 113.78, 110.75, 75.49, 45.69, 31.73, 31.25, 30.49, 30.23, 29.45, 29.30, 29.09, 27.06, 26.33, 22.68, 14.20. MS: m/z 1190.61 [M⁺]. Anal. calcd for C₇₄H₉₀N₆S₄ : C, 74.58; H, 7.61. Found: C, 74.18; H, 7.58.

(2E,2'E)-dihexyl3,3'-(5',5''-(5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-

diyl)bis(3,4'-dihexyl-2,2'-bithiophene-5',5-diyl))bis(2-cyanoacrylate) (DINI-CA): Hexyl 2-cyanoacetate (120 mmol) dissolved in CHCl₃ (40 mL) was added to **5a** (20 mmol) followed by 2 drops of piperidine. The reaction was stirred overnight at room temperature. The mixture was poured into water and extracted with dichloromethane. The organic layer was then dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel (dichloromethane : hexane = 1:1). The crude product was washed with hexane and MeOH to afford a deep red solid in 53% yield. ¹H NMR (300 MHz, acetone) δ 8.35(s, 1H), 7.99 (d, J = 7.5Hz, 1H), 7.86 (s, 1H), 7.68 (s, 1H), 7.40 (s, 1H), 7.31(dd, J = 7.5Hz, 1H), 4.66 - 4.71 (t, 2H), 4.26 - 4.31 (t, 2H), 2.93 - 2.98 (t, 2H), 2.85 - 2.90 (t, 2H), 1.76 - 1.78 (m, 8H), 1.33-1.49(m, 24 H), 0.85 - 0.96 (m, 12H). ¹³C NMR (75 MHz, CDCl₃) : δ 177.99, 177.42, 163.45, 159.13, 156.47, 147.06, 146.28, 143.02, 142.64, 140.90, 140.16, 139.45, 132.60, 132.47, 127.43, 126.97, 120.88, 116.33, 114.01, 97.26, 78.71, 66.66, 31.78, 31.55, 30.51, 29.49, 29.35, 29.12, 28.71, 27.08, 25.64, 22.78, 14.28. MS: m/z 1396.79 [M⁺]. Anal. calcd for C₈₆H₁₁₆N₄O₄S₄ : C, 73.88; H, 8.36. Found: C, 73.56; H, 8.30.

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2,2'-(5',5''-(5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-diyl)bis(3,4'-dihexyl-2,2'bithiophene-5',5-diyl))bis(methan-1-yl-1-ylidene)bis(1H-indene-1,3(2H)-dione)

(**DINI-Ind**): 1,3-Indandione (120 mmol) dissolved in CHCl₃ (40 mL) was added to **5a** (20 mmol) followed by 2 drops of piperidine. The reaction was stirred at room temperature. The mixture was poured into water and extracted with dichloromethane. The organic layer was then dried over anhydrous MgSO₄. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel (ethylacetate : hexane = 1:5). The crude product was washed with MeOH to afford a purple solid in 62% yield. ¹H NMR (300 MHz, THF) δ 7.99(s, 1H), 7.87 - 7.95 (m, 4H), 7.77 - 7.85 (m, 2H), 7.61 (s, 1H), 7.39 (s, 1H), 7.28 (d, J = 7.8Hz, 1H), 4.60 - 4.62 (t, 2H), 2.91 - 2.96 (t, 2H), 2.82 - 2.88 (t, 2H), 1.80 - 2.04 (m, 4H), 1.67 - 1.80 (m, 2H), 1.40-1.46(m, 18H), 0.90 - 0.96 (m, 9H). ¹³C NMR (400 MHz, THF) : δ 190.00, 189.79, 146.49, 143.33, 142.12, 141.79, 141.23, 140.36, 140.04, 135.81, 135.74, 134.10, 131.30, 125.13, 123.51, 120.76, 118.92, 115.12, 111.56, 46.11, 32.89, 32.19, 32.13, 31.51, 31.28, 30.81, 30.47, 30.23, 29.93, 27.91, 26.01, 25.88, 25.61, 25.29, 25.09, 23.74, 23.66, 14.62, 1.53. MS: m/z 1350.64 [M⁺]. Anal. calcd for C₈₆H₉₈N₂O₄S₄ : C, 76.40; H, 7.31. Found: C, 76.33; H, 7.27.

(5E,5'E)-5,5'-(5',5''-(5,10-dihexyl-5,10-dihydroindolo[3,2-b]indole-2,7-diyl)bis(3,4'dihexyl-2,2'-bithiophene-5',5-diyl))bis(methan-1-yl-1-ylidene)bis(3-ethyl-2-

thioxothiazolidin-4-one)(**DINI-Rho**): 3-Ethylrhodanine(100 mmol) and AcONH₄)dissolved in AcOH (40 mL) was added to **5a** (5 mmol). The reaction was refluxed overnight. Then the product were isolated by filtration and washed with H₂O and MeOH. The deep red product was dissolved in CHCl₃ and dried over anhydrous Na₂SO₄. After evaporation of the solvent, the residue was purified by column chromatography on a silica gel (dichloromethane : hexane = 2 : 3). The crude product was washed with hexane and MeOH to afford a red-purple solid in 74% yield. ¹H NMR (300 MHz, CD₂Cl₂) δ 7.88(d, J = 7.5 Hz, 1H), 7.81 (s, 1H), 7.56 (s, 1H), 7.30 - 7.32 (m, 2H), 7.24(s, 1H), 4.54 - 4.56 (t, 2H), 4.14 - 4.21 (q, 2H), 2.86 - 2.91 (t, 2H), 2.78 - 2.84 (t, 2H), 2.00 - 2.03 (t, 2H), 1.70 - 1.74 (m, 4H), 1.27-1.41(m, 18H), 0.85 -0.94 (m, 12H). ¹³C NMR (400 MHz, CDCl₃) :192.41, 185.87, 184.43, 168.22, 150.46, 138.90, 130.61, 125.97, 40.12, 31.95, 31.85, 30.52, 29.92, 29.58, 29.44, 27.14, 22.87, 22.84, 22.78, 14.31, 14.24, 12.52. MS: m/z 1380.56 [M⁺]. Anal. calcd for C₇₈H₁₀₀N₄O₂S₈ : C, 67.78; H, 7.29. Found: C, 67.53; H, 7.22.

Device fabrication and characterization

The small molecule BHJ OSCs were fabricated with configuration of ITO coated glass /PEDOT:PSS/donors:PC₇₁BM/Al using a conventional solution spin coating method. The indium tin oxide (ITO) coated glass substrates were cleaned subsequently by ultrasonic treatment in detergent, deionized water, acetone and isopropyl alcohol for 20 min. A layer of PEDOT:PSS was spin coated (3500 rpm, ~40 nm) onto ITO coated glass substrate and baked at 120 °C for 20 min. The active layer was spin coated onto the top of PEDOT:PSS layer from the different weight ratios of donors and $PC_{71}BM$ in dichlorobenzene (DCB) at 1500 rpm for 25 s. For two step annealing (TSA) treatment, the optimized active layer was thermally annealed by placing the active layer on hot plate at 110 °C for 5 min and then cooled up to room temperature. The subsequent solvent vapor annealing (SVA) and the active layer was place in a glass Petri dish containing 200 µL THF. The thickness of the active layers is about 90 \pm 5 nm. Finally 50 nm aluminum (Al) layer was deposited onto the top of active layer under the high vacuum by a shadow mask. The effective area of each device is about 20 mm². The hole-only and electron-only devices with ITO/PEODT:PSS/active layer/Au and ITO/Al/active layer:PC₇₁BM/Al architectures were also fabricated in an analogous way in order to measure the hole and electron mobility, respectively. The currentvoltage characteristics of BHJ organic solar cells were measured using a computer controlled

Keithley 238 source meter under simulated AM1.5G, 100 mW/cm². A xenon light source coupled with optical filter was used to give the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured at illuminating the device through the light source and monochromator and the resulting current was measured using a Keithley electrometer under short circuit condition.

Results and discussion

Optical and electrochemical properties

The normalized absorption spectra of the four small molecules in dilute DCB solution and thin films are shown in Figure 1a and 1b, respectively. The corresponding data are summarized in Table 1. All the small molecules showed two absorption bands covering the wavelength range from 350 to 650 nm. The absorption band in high energy and low energy wavelength regions are attributed to localized π - π * transitions and intramolecular charge transfer (ICT) transitions between central donor and terminal acceptor units, respectively. It can be seen from the Figure 1a that the absorption peak assigned to high energy band for all small molecules is almost same, but the absorption peak assigned to ICT bands are different due to the different electron accepting ability of end group units. The bathochromic shift following the trend **DINI-IND>DINI-DCV>DINI-Rho>DINI-CA** is in agreement with the electron accepting ability of IND>DCV>Rho>CA. This indicates that the small molecule having stronger electron withdrawing moiety exhibits a red-shift absorption spectra due to its stronger ICT [12]. The absorption spectra of all small molecules in thin film show broad and bathochromic shift of ICT absorption band compared to their corresponding solution spectra, indicating that these molecules follow J aggregates in film state and increased intermolecular interactions and backbone planarity in the solid state [13]. Moreover, all the small molecules showed a vibronic shoulder, indicating the existence of strong π - π stacking between the molecule backbones. The optical bandgap of these small molecules were estimated from the absorption edges in thin film spectra of corresponding small molecules to be 1.78 eV, 1.95 eV, 1.74 eV, and 1.88 eV for **DINI-DCV**, **DINI-CA**, **DINI-IND** and **DINI-Rho**, respectively.

The highest occupied molecular orbital (HOMO) energy level of SMs was estimated from the onset oxidation potential of corresponding cyclic voltammogram (shown in Figure S13, supplementary information) with the assumption that the energy level of ferrocene (F_c) was 4.8 eV below the vacuum level. The LUMO energy level of the small molecules was estimated according to $E_{LUMO}=E_{HOMO}+E_{o-o}$, where E_{o-o} is determined from the intersection of absorption and emission spectra in solution (as shown in Figure S14, supplementary

information). The estimated HOMO/LUMO energy levels for small molecules are compiled in Table 1. It is well known that the HOMO and LUMO energy levels are affected by the electron donating and withdrawing units in D-A type compounds, respectively. Similar value of LUMO energy level for **DINI-DCV** and **DINI-IND** indicates that DCV and IND have almost same electron withdrawing ability. The LUMO energy level of these small molecules is sufficiently higher than the LUMO of $PC_{71}BM$ (-4.1 eV), indicating that the efficient photoinduced charge separation is possible and can be used as donor for BHJ organic solar cells.

Figure 2 shows the optimized structure of **DINI-CA**, **DINI-Rho**, **DINI-DCV** and **DINI-IND**, which are calculated by the time dependent density functional theory (TD-DFT) using B3LYP functional/3-21 G* basis set. The orbital density of the HOMO of these small molecule are similarly observed in both DINI and thiophene bridge. However, the LUMO is located predominantly in the different electron accepting end group units and thiophene bridge, showing a general orbital distribution of D-A small molecules.

Photovoltaic properties

In order to achieve the high PCE of organic BHJ solar cells, there should be a balance between the absorbance and charge transport ability of active layer. The weight ratio of small molecule donors and $PC_{71}BM$ were varied from 1:05 to 1:2.5 and devices with the ratio 1:2 showed the maximum PCE. The current-voltage (J-V) characteristics of the BHJ organic solar cells based on DINI-DCV, DINI-CA, DINI-Rho and DINI-IND as donor and PC71BM acceptor with optimized D/A weight ratio (1:2) are shown in Figure 3a. The corresponding photovoltaic parameters are compiled in Table 2. The device based on **DINI-IND**:PC71BM showed highest PCE of 3.04 % with J_{sc} of 7.20 mA/cm², V_{oc} of 0.88 V and FF of 0.48, whereas the device based on DINI-CA:PC71BM showed the lowest PCE of 1.63 % with Jsc of 4.98 mA/cm², V_{oc} of 0.78 V and FF of 0.42. It can be seen from the table 2 that the device based on **DINI-DCV** showed highest V_{oc}, due to the its deeper HOMO level compared to other, since the V_{oc} of the BHJ OSC is directly related to the difference between the LUMO of acceptor and HOMO of donor used in the active layer. The variation of J_{sc} of the OSCs is consistent with the absorption spectra of active layer and IPCE spectra of the devices (Figure 4). The J_{sc} estimated from the integration of the IPCE spectra are compiled in Table 2 and matched with the J_{sc} obtained from J-V characteristics measurements.

The low values of PCE based on these small molecules is mainly attributed to the low values of both J_{sc} and FF and related to the poor morphology of active layer, since the nanoscale phase separation is needed for the efficient exciton dissociation and charge

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transport. Two step annealing (TSA) approach that combines thermal and solvent vapor annealing has been adopted to tune the morphology of the active layer using polymers and small molecules as donor [14] and found that the PCE has been significantly improved. We have examined the effect of TSA for devices employing all the small molecules and found that all the devices showed the increase in PCE (see the table 2), but **DINI-DCV** and **DINI-IND** showed the higher PCE than other two molecules. Therefore, we have discussed the effect of TSA only for the devices based on **DINI-DCV** and **DINI-IND** in detail and the J-V characteristics of these devices under illumination intensity of 100 mW/cm² are shown in Figure 5a. The PCE was improved up to 7.04 % (J_{sc} =12.18 mA/cm², V_{oc} = 0.85 V and FF= 0.68) and 6.16 % (11.74 mA/cm², $V_{oc} = 0.86$ V and FF= 0.61) for **DINI-IND** and **DINI-DCV**, respectively, with remarkably enhanced Jsc and FF. The significant improved PCE originates from the favorable morphological evolution in the active layer induced by the combined effect of thermal and solvent vapor annealing. The IPCE spectra of the devices are shown in Figure 5b. The IPCE peak of both **DINI-DCV** and **DINI-IND** was significantly enhanced after the TSA treatment (see Figure 3b and 5b), contributing to higher J_{sc} . Moreover, the IPCE spectra of the devices based on the TSA treated active layer shows broader response and redshift as compared to the devices without TSA, which is consistent with their absorption spectra (Figure 4). The increase in the absorption intensity and broadening of absorption profile towards longer wavelength region of blended film upon TSA treatment may be related to the improved the π - π stacking and planarity of donor.

To get information about the reason behind the improvement in the PCE of the devices by the TSA treatment, X-ray diffraction (XRD) measurement was applied to explore the molecular packing in these active layers (Figure 6). As shown in Figure 6, as cast **DINI-DCV**:PC₇₁BM and **DINI-IND**:PC₇₁BM film show a weak (100) diffraction peak located at 2θ =3.96° and 4.22°, corresponding to the d-spacing of 2.33 nm and 2.18 nm, respectively, between the molecular layers. This suggests that **DINI-IND** forms a denser molecular packing than **DINI-DCV** counterpart may induce a better nano-phase separation between .donor and acceptor in the as cast blend film, may be responsible for the higher PCE for device based on **DINI-IND**. After TSA, the (100) peak shifts to 2θ =4.26° and 4.45° for **DINI-DCV** and **DINI-IND**, respectively and also becomes much stronger, indicating an improved layer packing molecules existing in the active layer. The increased in the diffraction intensity for TSA treated blended films indicates that the degree of crystallinity was significantly improved as compared to as cast counterpart. The combined effect of thermal

annealing and subsequent solvent vapor annealing promotes the nanoscale morphology in the active layer for efficient charge transfer and transportation, resulting in an improvement in J_{sc} and FF.

The morphological change in the active layer with TSA treatment has been further investigated by transmission electron microscopy (TEM). Figure 7 shows the TEM images of **DIN-DCV**:PC₇₁BM and **DIN-IND**:PC₇₁BM blended films with and without TSA treatment. The bright and dark regions correspond to donors and PC₇₁BM domains, respectively [15]. The blended film cast from CB showed very uniform and homogeneous morphology, owing to the good miscibility of donors and PC₇₁BM. Desirable nano-phase with separated donor and acceptor domains is not observed, resulting in low J_{sc} and FF and overall PCE. However, upon TSA treatment of active layer, the domain size of both donor and PC₇₁BM becomes bigger and a nanoscale phase separation is developed as shown in Figure 7, consequently leading to a significant improvement in the photovoltaic performance of devices.

On organic solar cells using BHJ active layer, hole and electron mobilities are important parameters to ensure the efficient charge carrier transport towards the electrodes and to suppress the photocurrent loss by competing charge recombination. Moreover, balance between the hole and electron mobilities in the active layer is also important for improving J_{sc} and FF of the OSCs. The hole mobilities of the blended films with and without TSA were measured by the space charge limited current method [16], with hole only device structure ITO/PEDOT:PSS/active layer/Au, as shown in Figure 8. The hole mobilities are 0.98 x10⁻⁵ and $1.45 \times 10^{-5} \text{ cm}^2/\text{Vs}$ for as cast **DINI-DCV** and **DIN-IND**, respectively. After the TSA, the mobilities increase to 8.98 $\times 10^{-5}$ and 1.16 $\times 10^{-4}$ cm²/Vs for **DINI-DCV** and **DIN-IND**, respectively. We have also measured the electron mobilities using the electron only device structure ITO/Al/active layer/Al using same SCLC method and found that electron mobilities is in the range of 2.42-2.48 $\times 10^{-4}$ cm²/Vs for both as cast and TSA treated blended films. The relatively unbalanced carrier mobilities (ratio of electron to hole mobilities are 24.69 and 16.7 for **DINI-DCV** and **DIN-IND**, respectively) for as cast films can be ascribed to the poor morphology which results in the lower photovoltaic performance. The increase in hole mobility in the blend film with the TSA treatment leads to the more balanced charge transport (electron to hole mobilities are 2.76 and 2.14 for **DINI-DCV** and **DIN-IND**, respectively), enhancing the FF and overall PCE. The high hole mobility and better charge transport for the devices processed with TSA treated active layers is consistent with the increase in crystallinity of the active layer, and molecular packing as illustrated by XRD and TEM measurements. Therefore TSA treatment resulted much enhanced hole mobility together with considerably better balanced hole and electron mobility which led to a much higher charge carrier extraction efficiency and thus responsible for higher FF [17]. DINI-IND:PC₇₁BM based device achieved FF value of 0.68, which may be associated with its high and balanced charge carrier mobility and well as lower charge recombination losses [18].

The relationship between the photocurrent (J_{ph}) and effective voltage (V_{eff}) was investigated for the devices with and without TSA treated DINI-DCV:PC71BM and DINI-**IND**:PC₇₁BM layers and shown in Figure 9. Here, J_{ph} is defined as $J_{ph} = J_L - J_D$, where J_L and J_D are the current densities under illumination and in the dark, respectively, $V_{eff} = V_o - V_{appl}$, where V_o is the voltage at which J_{ph}=0 and V_{appl} is applied voltage [19]. In the devices based on the TSA treated active layer, J_{ph} shows a linear dependence at the low V_{eff} and saturated at a high V_{eff} . The devices based on the without TSA treated active layers also showed a linear J_{ph}- V_{eff} dependence at low values of V_{eff}, but does not fully saturate even at high voltage. The V_{eff} value corresponds to an internal electric field to sweep out the photogenerated charge carriers in the active layer towards the electrodes. It means that much stronger electric field is required to seep out photogenerated charges and suggest relative poor charge transport within the active layer. It is consistent with the absence of ordered domains to provide effective percolation pathways for charge carriers in the active layer. The saturation current density (J_{sat}) is higher for the devices prepared with TSA treated active layers which is higher than corresponding as cast counterparts. It means that the TSA active layer based device has a higher maximum exciton generation rate (G_{max}). G_{max} is given by J_{sat}=qG_{max}L, where L is the thickness of the active layer. The higher G_{max} reflects the higher photon absorption which is consistent with the absorption profile of TSA treated active layer (Figure 4). We have also estimated the charge collection probability (P_c) in the devices processed with as cast and TSA treated active layers, $P_c = J_{sc}/J_{phsat}$ [20] and the values are 0.54, 0.56 0.82, and 0.84 for as cast DINI-DCV:PC71BM, DINI-IND:PC71BM, TSA treated DINI-DCV:PC71BM and DINI-IND:PC₇₁BM based devices, respectively. Therefore, the enhanced J_{sc} in the TSA treated active layer based OSC is attributable to the enhanced light absorption and light harvesting in the active layer and efficient charge collection.

Conclusions

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We have designed and synthesized four A-D-A small molecules with common central dihydroindoloindole (DINI) donor unit, different acceptor end groups such as dicyanovinylene (DCV), indenedione (IND), cyanoacrylate (CA) and rhodanine (Rho) linked

through bi-thiophene as π -linkers denoted as **DINI-DCV**, **DINI-IND**, **DINI-CA** and **DINI-Rho** and their optical and electrochemical properties were investigated. These small molecules were used as electron donors along with PC71BM as acceptor of solution processed small molecule OSCs. After the optimization of donor to acceptor weight ratio, spinning speed and concentration, the 1:2 weight ratio showed the best photovoltaic performance for all small molecules. The OSCs based on **DINI-CA**:PC₇₁BM, **DINI-**DCV:PC71BM, DINI-Rho:PC71BM and DINI-IND:PC71BM spin cast from DCB showed the PCE of 1.63 %, 2.53 %, 2.13 % and 3.04 %, respectively, indicating that acceptor end group has impact on the overall PCE. In order to improve PCE further, we have employed a simple TSA (combined thermal annealing and subsequent solvent vapor annealing) treatment of active layer method and the PCE has been improved significantly (7.04 % and 6.16 % for **DINI-IND:** $PC_{71}BM$ and **DINI-DCV:** $PC_{71}BM$, respectively) which is ascribed to the better nanophase morphology, crystallinity, molecular packing and light harvesting ability of active layers, induced by the TSA treatment. These combined properties enhance the exciton generation efficiency and relatively better balanced charge transport, leading to the improvement in J_{sc}, FF and PCE of resulted OSCs.

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Compounds	$\lambda_{abs}^{[a]}/nm (\epsilon/M^{-1}cm^{-1})$	λabs(nm) (film)	E_g^{opt} (eV)	$\lambda_{PL}^{[a]}/nm$	E ₀₋₀ (eV)	E _{HOMO} (eV) ^b	E _{LUMO} (eV) ^c
DINI-DCV	400 (31 899) 514 (46 703)	572	1.74	736	2.03	-5.14	-3.11
DINI-CA	395 (44 325) 488 (61 865)	534	1.95	722	2.04	-4.96	-2.92
DINI-IND	397 (28 536) 528 (50 068)	595	1.68	736	2.00	-5.12	-3.12
DINI-Rho	399 (38 089) 503 (60 243)	562	1.88	720	2.02	-5.08	-3.06

 Table 1 Optical and redox parameters of the compounds.

[a] UV-vis absorption spectra and fluorescence spectra were measured in Chlorobenzene solution. [b] Redox potential of the compounds were measured in CH₂Cl₂ with 0.1M (*n*-C₄H₉)₄NPF₆ with a scan rate of 100 mVs⁻¹ (*vs*. Fc/Fc⁺). [c] E_{LUMO} = E_{HOMO} + E_{gap} [d] E_{gap} was calculated from the intersection of absorption and emission spectra in solution

Table 2 Photovoltaic parameters of organic solar cells based on **DINI-DCV**, DINI-CA, DINI-Rho and DINI-Ind as donor and $PC_{71}BM$ (optimized weight ratio 1:2)

Active layer	J_{sc}	Jsc	V _{oc}	FF	PCE (%)
5	(mA/cm^2)	(mA/cm	(V)		(PCE _{average})
		$(2)^{c}$			
DINI-CA:PC ₇₁ BM ^a	4.98	4.91	0.78	0.42	1.63 (1.59)
DINI-DCV:PC ₇₁ BM ^a	6.12	6.04	0.90	0.46	2.53(2.48)
DINI-Rho:PC ₇₁ BM ^a	5.64	5.55	0.86	0.44	2.13 (2.07)
DINI-IND:PC ₇₁ BM ^a	7.20	7.26	0.88	0.48	3.04(3.98)
DINI-CA:PC ₇₁ BM ^b	7.30	7.23	0.75	0.54	2.95(2.86)
DINI-DCV:PC71BMb	11.74	11.65	0.86	0.61	6.16(6.12)
		11100	0100	0.01	0110(0112)
DINI Dhade DMb	11.09	10.08	0.82	0.58	5 22 (5 18)
	11.08	10.96	0.82	0.38	5.25 (5.16)
	10.10	10.00	0.95	0.00	7.04(6.00)
DIMI-IND:PC71BM	12.18	12.25	0.85	0.08	7.04(6.98)

^aAs cast

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^bTSA treated active layer

^cEstimated from IPCE spectra



Scheme 1 Synthesis of DINI-DCV, DINI-CA, DINI-IND and DINI-Rho small molecules



Figure 1 Normalized absorption spectra of DINI-DCV, DINI-CA, DINI-IND and DINI-Rho (a) dilute DCB solution and (b) thin film cast from DCB solution.



Figure 2 Isodensity surface plots of (a) **DINI-DCV** and (b) **DINI-CA** and (c) **DINI-Ind** and (d) **DINI-Rho**, calculated by the time dependent-density functional theory (TD-DFT) using the B3LYP functional/6-31G* basis set.



Figure 3 (a) Current –voltage characteristics under illumination and (b) IPCE spectra of devices based on optimized active layers of small molecule donors and $PC_{71}BM$ acceptor cast from CB solution.

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Figure 4 Normalized absorption spectra of as cast (CB) and TSA treated DINI-DCV:PC₇₁BM and DINI-IND :PC₇₁BM and TSA treated active layers



Figure 5(a) Current –voltage characteristics under illumination and (b) IPCE spectra of the OSCs based on TSA treated **DINI-DCV**:PC₇₁BM and **DINI-IND**:PC₇₁BM blends.



Figure 6 XRD patterns of the as cast and TSA treated blended active layers



Figure 7 TEM images (a) **DINI-DCV**:PC₇₁BM (as cast) (b) **DINI-DCV**:PC₇₁BM (TSA), (c) **DINI-IND**:PC₇₁BM (as cast) and (d) **DINI-IND**:PC₇₁BM (TSA), scan bar is 200 nm



Figure 8 Current- voltage characteristics of hole only devices to estimate the hole mobilities in the as cast and TSA treated active layers



Figure 9 Variation of J_{ph} with effective voltage (V_{eff}) for the OSCs based on as cast and TSA treated active layers

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The optimized device after TSA treatment showed PCE of 7.04 % and 6.16 % **DIN-IND**:PC₇₁BM (1:2) and **DIN-CN**:PC₇₁BM (1:2), respectively