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PII: S0143-7208(19)30672-2

DOI: https://doi.org/10.1016/j.dyepig.2019.107677

Article Number: 107677

Reference: DYPI 107677

- To appear in: Dyes and Pigments
- Received Date: 26 March 2019
- Revised Date: 20 June 2019
- Accepted Date: 26 June 2019

Please cite this article as: Rao PS, More VG, Jangale AD, Bhosale SV, Bhosale RS, Puyad AL, Chen J-Y, Li J-L, Bhosale SV, Gupta A, Sharma GD, A series of V-shaped small molecule non-fullerene electron acceptors for efficient bulk-heterojunction devices, *Dyes and Pigments* (2019), doi: https://doi.org/10.1016/j.dyepig.2019.107677.

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Non-fullerene electron acceptors NDICz-4, NDICz-5 and NDICz-6

A series of V-shaped small molecule non-fullerene electron acceptors for efficient bulk-heterojunction devices

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Abstract

Two simple semiconducting acceptor-acceptor₁-donor-acceptor (A-A₁-D-A) modular, small molecule non-fullerene electron acceptors, 2-(4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-3-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)ethynyl)-9-octyl-9*H*-carbazol-3-yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**NDICz-5**) and <math>2-(4-(3,3-dicyano-2-(4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetraoxo-3,6,7,8-tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetr

tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-yl)phenyl)ethynyl)-9-octyl-9H-carbazol-3yl)allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (NDICz-6), designed, were synthesized and characterized for application in solution-processable bulk-heterojunction solar cells. The optoelectronic and photovoltaic properties of NDICz-5 and NDICz-6 were directly compared with those of a structural analogue, 7,7'-(((9-octyl-9H-carbazole-3,6diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(2-hexadecylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (NDICz-4), which was designed based on an A-D-A format. All of these new materials were designed to be V-shaped and comprised an electron rich carbazole donor core (D) together with electron deficient naphthalene diimide terminal core (A). In the simple A-D-A system, naphthalene diimide was the terminal functionality, whereas in the A-A₁-D-A system, tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) derived functionalities were incorporated as A₁ units by keeping D/A units constant. The inclusion of A₁ was mainly done to induce cross-conjugation within the molecular backbone and hence to improve light-harvesting. The physical and optoelectronic properties were characterized by ultraviolet-visible, thermogravimetric analysis, photo-electron spectroscopy in air and cyclic voltammetry. These new materials exhibited energy levels complementing those of the conventional donor polymer poly(3-hexyl thiophene) (P3HT). Solution-processable bulk-

heterojunction devices were fabricated with NDICz-4, NDICz-5 and NDICz-6 as nonfullerene electron acceptors. Studies on the photovoltaic properties revealed that the best P3HT: NDI-Cz6-based device showed an impressive enhanced power conversion efficiency of 7.58%, an increase of around two-fold with respect to as-cast blend, after solvent vapor annealing using carbon disulfide. Not only are the results among the best in the current literature using the conventional donor polymer P3HT, but clearly demonstrate that A-A₁-D-A type, V-shaped small molecules are promising non-fullerene acceptors in the research field of organic solar cells.

Keywords: Non-fullerene; V-shaped; solution-processable; tetracyanoethylene; carbazole; tetracyanoquinodimethane

1. Introduction

The constant demand for the development of renewable energy technologies is a pressing need for society. The natural resources such as wind, sunlight and water can provide a definitive answer. However, technologies based on harvesting solar energy at an affordable price are highly promising. The technologies such as organic (otherwise termed bulk-heterojunction) solar cells are the most studied, well understood and widely accepted strategies given the advantages, such as lightweight, flexibility and low-cost, they offer [1–8]. The development of such devices has seen advancements in the areas of new material design and fabrication strategies. In terms of materials' advancement, non-fullerene acceptors have been developed over the past few years as they are seen to hold multiple advantages such as strong light-harvesting, easily tunable energy levels, improved morphological stability, and facile synthetic manipulations. The current literature indicates that a variety of structural

arrangements have been used to design efficient non-fullerene acceptors, and to improve power conversion efficiency (PCE) in particular [9–37].

In 2016, Hou et al. reported 12% PCE for bulk-heterojunction (BHJ) solar cells based on methyl-modified dicycanovinylindan-1-one non-fullerene acceptor [38]. The same group recently achieved a PCE of 13% based on devices fabricated using a combination of PBDB-T-SF and IT-4F [39]. Such literature clearly indicates that one can easily tune optical and electrochemical properties of small molecule non-fullerene electron acceptors using organic synthetic strategies [40-42]. Particularly, nonfullerene acceptors based on donor-acceptor (D-A) subunits are attractive due to their feasibility to tune electronic energy levels, absorption properties, solubility in common organic solvents and self-assembly behaviour. Among the reported non-fullerene acceptors based on D-A format, target structures using naphthalene diimide (NDI) unit are very promising given the capacity of such targets to accept electrons. Moreover, the advantages of using NDI in a given target can be realised in terms of its interesting physical and electronic properties, strong electron-withdrawing strength, and the capacity to tune its solubility via incorporating lipophilic chains on nitrogen atoms [43–44]. Keeping such criteria in mind, researchers have developed a number of NDI-based target materials, and in particular non-fullerene acceptors, for organic solar cell applications. Such targets have been generated by functionalization of NDI unit either at imide position or at the central core.

Marder *et al.* reported pyrrole[3,2-*d*:4,5-*d'*]bisthiazole-bridged bis(naphthalene diimide)s as electron-transport materials for organic field-effect transistor (OFET) applications [45]. Patil *et al.* reported the OPV performance of DPP-NDI-DPP derivative as non-fullerene electron-acceptor and achieved a PCE of 1.02% [46]. Russell and co-workers synthesized NDI-based dimer, where NDIs were linked with vinyl bridge, which

exhibited 2.41% PCE [47]. Kim *et al.* have demonstrated an encouraging PCE of 3.01% with an open circuit voltage (V_{oc}) of 0.75 V using NDI derivative NDICN-TVT [48]. The NDI core has further been modified with the use of a number of electron withdrawing groups, such as rhodanine, 1,3-indanedione, 2-methoxyethyl-2-cyanoacetate and cyanopyridone, so as to improve device performance [49–50]. We have recently demonstrated the use of TPA-NDI-C₆₀ triad as a D-A-A system with spectacular PCEs of 3.03% and 4.85%, respectively, before and after annealing [51]. Samuel *et al.* reported NDI-based imide substituted derivatives as electron acceptor materials for BHJ applications [52]. However, less attention has been given to the design and develop of those NDI derivatives which boast functionalization at the imide position.

Our group recently reported a PCE of 2.3% for a non-fullerene electron acceptor based on central carbazole (Cz) and terminal diketopyrrolopyrrole (DPP) units [53]. It is well documented that Czs are extensively utilized as electron donor materials, providing good charge transport abilities for various applications. Würthner *et al.* reported coreextension of NDI with two annulated indole rings leading to carbazolo[2,3-*b*]carbazole diimides (CbDIs) and its application in OFETs with mobility values up to 0.2 cm²/(V s) [54]. Li and co-workers also demonstrated Cz-based polymers and their photovoltaic properties [55]. On the other hand, tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) units are very strong electron accepting building blocks with high electron mobility that have been extensively employed to functionalize acceptor molecules [56]. Small molecule non-fullerene electron acceptors comprising TCNE and TCNQ units have not been extensively investigated, with the exceptions reported by Mishra and co-workers, which showed impressive PCEs [57]. In 2017, we developed TPA-based small molecule non-fullerene electron

acceptors containing TCNE and TCNQ functionalities for BHJ solar cell applications, with good to moderate efficiencies of 2.28% and 3.75% [58].

Taking into account of advantages exhibited by NDI moiety and the literature precedence where NDI, Cz, and TCNE and TCNQ units have been used for organic photovoltaic applications, herein we report the design, synthesis and characterization of three novel non-fullerene acceptors, 7,7'-(((9-octyl-9*H*-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(2-hexadecylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone)

(**NDICz-4**), 2-(4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-

 $tetrahydrobenzo[\mathit{lmn}][3,8] phenanthrolin-2(1H)-yl) phenyl)-3-(6-((4-(7-hexadecyl-1,3,6,8-(1-y))-3-(6-(1-y))-3-(1-y))$

tetraoxo-3, 6, 7, 8-tetrahydrobenzo [lmn] [3, 8] phenanthrolin-2(1H)-yl) phenyl) ethynyl)-9-octyl-line (lmn) [3, 8] phenanthrolin-2(1H)-yl) phenyl) ethynyl) ethynyl ethynyl) ethynyl) ethynyl ethynyl ethynyl ethynyl) ethynyl) ethynyl) ethynyl ethyn ethyn

9H-carbazol-3-yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (NDICz-5) and 2-(4-(3,3-dicyano-

2-(4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-

yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-

tetrahydrobenzo[*lmn*][3,8]phenanthrolin-2(1*H*)-yl)phenyl)ethynyl)-9-octyl-9*H*-carbazol-3yl)allylidene)cyclohexa-2,5-dien-1-ylidene)malononitrile (**NDICz-6**), where **NDICz-4** is based on an A-D-A format, and **NDICz-5** and **NDICz-6** are based on A-A₁-D-A modular design. We introduced TCNE and TCNQ functionalities in **NDICz-5** and **NDICz-6**, respectively, which served as A₁ units so as to generate the latter module. The common donor core (D) was Cz and the terminal acceptor unit (A) was NDI. It was observed that the introduction of TCNE and TCNQ functionalities in A-A₁-D-A system resulted in strong intramolecular charge transfer transition when compared with A-D-A system. The introduction of TCNQ in particular exhibited a broader absorption profile which can be ascribed to the stronger electron withdrawing nature of TCNQ relative to TCNE. Solutionprocessable BHJ devices were fabricated with **NDICz-4**, **NDICz-5** and **NDICz-6** as nonfullerene electron acceptors. Studies on the photovoltaic properties revealed that the best

P3HT: **NDICz-6**-based device showed an impressive PCE of 7.58% after solvent vapor annealing (SVA) using carbon disulfide. The increase in efficiency after SVA treatment was around two-fold when compared with as-cast blend as well as P3HT: **NDICz-4**-based devices. To the best of our knowledge, there are no reports on the conjoint use of Cz and NDI functionalities where such functionalities have been used to design V-shaped non-fullerene acceptors comprising either TCNE or TCNQ units. Our results clearly indicate that these A-A₁-D-A-based small molecules are potential acceptors for efficient organic solar cells using the commercially available donor polymer P3HT and can further be explored with a variety of donors. The molecular structures of the investigated materials are represented in Fig. 1.

>Fig. 1<

2. Experimental Details

2.1. Materials, methods and device details

All the reagents and chemicals used, for example naphthalene dianhydride, hexadecane amine, carbazole, 1-bromooctane, sodium hydride, *N*-iodosuccinimide, triethylamine, copper iodide, (trimethylsilyl)acetylene, tetrakis(triphenylphosphine)palladium(0), TCNE and TCNQ, to name a few, unless otherwise specified, were purchased from Sigma-Aldrich Co., Bengaluru, Karnataka, India, and were used without any purification. AR grade solvents were purchased from Finar chemicals Limited, India and used as received. The intermediates and target materials were purified using silica gel chromatography.

FT-IR spectra were measured on a Thermo Nicolet Nexus 670 spectrometer using KBr pellets. ¹H and ¹³C NMR spectra were recorded at 400 or 500 MHz as indicated. ¹H and ¹³C chemical shifts were calibrated using residual non-deuterated solvent as an internal reference and are reported in parts per million (δ) relative to tetramethylsilane ($\delta = 0$). ESI-MS data

was taken on Shimadzu lab solutions. For MALDI-TOF measurements, a Schimadzu Biotech Axima performance spectroscopic instrument were used. Differential scanning calorimetry (DSC) analysis was performed using a TA Instruments Q-100 DSC with a heating rate and a cooling rate of 10 °C per minute. Thermogravimetric analysis (TGA) measurement was performed using a TA instruments Q-500 TGA under flowing nitrogen gas at a heating rate of 10 °C per minute. The UV-vis absorption spectra were recorded in a 1 cm path-length quartz cell using Shimadzu UV-1800 spectrophotometer. Fluorescence spectra were recorded using Shimadzu model R-6000 spectrofluorometer. Cyclic voltammetry measurements were recorded under nitrogen in a deoxygenated solution of tetra-n-butylammonium hexafluorophosphate (0.1 M) in dichloromethane or 1,2-dichlorobenzene using a PowerLab ML160 potentiostat interfaced via a PowerLab 4/20 controller to a PC running E-Chem for Windows version 1.5.2. Cyclic voltammograms (potential scan rate of 50 mV/s) and all measurements were carried out at room temperature using a three-electrode configuration consisting of a platinum working electrode; a platinum wire auxiliary electrode; and a nonaqueous Ag/AgCl reference electrode. PESA measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power number of 0.5. Samples for PESA were prepared on ITO cleaned glass substrates and were run using a power setting of 10 nW.

Organic solar cells were fabricated using the conventional architecture, ITO/PEDOT: PSS/P3HT: NDICz-4 or NDICz-5 or NDICz-6 /PFN /Al. Indium tin oxide (ITO) coated glass substrates were cleaned sequentially by 10 minutes ultrasonication in detergent, deionized water, acetone and isopropyl alcohol followed by drying in a nitrogen flow. The substrates were further dried at ambient conditions. The PEDOT: PSS solution was filtered and spin coated onto the pre-cleaned ITO substrates at 3500 rpm for 30 s and then annealed at 120 °C for 10 minutes. The blends of P3HT and acceptors (different weight ratios of donor and acceptor, total concentration 14 mg/mL) were dissolved in chloroform (CF). The

solutions were spin coated atop the PEDOT:PSS surface at 2000 rpm for 60 s and the samples were dried in a vacuum oven at 40 °C. A thin layer of PFN was spin coated on top of the active layer, which was dissolved in methanol and mixed with acetic acid with a concentration of 0.5 mg/mL and then spin coated at a rpm of 2000 to get a thin film of about 10 nm. Finally, the aluminium (Al) electrode was deposited on top of the active layer by thermal evaporation under a vacuum of 10^{-5} Torr. The current-voltage characteristics of the devices were measured using a computer-controlled Keithley 2400 source meter under stimulated AM 1.5 G at an intensity of 100 mW/cm² provided by a solar simulator. The incident photon to current conversion efficiency of the devices was measured by illuminating the device through the light source and the monochromator, and the resulting current was measured using a Keithley electrometer.

2.2. Synthetic details

>Scheme 1<

Compound **NDICz-4** was synthesized by reacting 3,6-diethynyl-9-octyl-9*H*-carbazole (compound **4**) with 2-hexadecyl-7-(4-iodophenyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone (compound **5**) using Sonogashira coupling reaction in dry tetrahydrofuran (THF) (Scheme 1). Compounds **NDICz-5** and **NDICz-6** were synthesized by reacting **NDICz-4** with TCNE and TCNQ, respectively (Scheme 2). The final compounds were purified using silica gel chromatography, characterized spectrally, and their optoelectronic properties were investigated. The materials were prepared in moderate to high yields and were found to be highly soluble in a variety of conventional organic solvents such as chlorobenzene, chloroform, dichloromethane and toluene. High solubility of organic

materials is an essential criterion for the fabrication of solution-processable organic photovoltaic devices and newly designed materials **NDICz-4**, **NDICz-5** and **NDICz-6** fulfil this criterion. Compound **5** was synthesized following the procedures reported in the literature (J Org Chem 2013;78:5227–38).

>Scheme 2<

2.2.1. 9-Octyl-9H-carbazole (1)

Carbazole (3 g, 17.9 mmol) and 1-bromooctane (9.3 mL, 53.8 mmol) were dissolved in dry DMF (40 mL) in a 100 mL round bottom flask with magnetic stirring bar. Sodium hydride (1.29 g, 53.8 mmol, 60 % dispersion in mineral oil) was added slowly at room temperature and the resulting suspension was refluxed overnight. After completion of reaction, excess NaH was quenched by adding methanol dropwise. The resulting reaction mixture was poured on ice and extracted with dichloromethane. The organic layer was separated, washed with water twice followed by brine and recovered to get a viscous brown liquid which was purified by column chromatography on silica gel using hexane as an eluent; yield = 4.55 g, 91 %. ¹H NMR (500 MHz, CDCl₃) δ = 8.10 (d, *J* = 7.7 Hz, 2H), 7.47 (t, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 2 H), 4.31 (t, *J* = 7.3 Hz, 2H), 1.89–1.84 (m, 2H) 1.40–1.23 (m, 10H), 0.86 (t, *J* = 6.7 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ = 140.77, 125.70, 122.74, 120.48, 118.53, 108.80, 43.17, 31.98, 29.91, 29.55, 29.36, 29.12, 27.48, 22.80, 14.27; ESI-MS (m/z) [M+H]⁺: 280.25.

2.2.2. 3,6-Diiodo-9-octyl-9H-carbazole (2)

Compound 1 (3 g, 10.7 mmol) was dissolved in a mixture of chloroform and acetic acid (30 mL; 1: 1) and the reaction vessel was covered with aluminum foil. *N*-iodosuccinimide (4.85

g, 21.5 mmol) was added and the reaction mixture was stirred for 12 h. After the consumption of starting material, the reaction mixture was diluted with chloroform (50 mL) and water (100 mL). The organic layer was separated, washed with water followed by 20% sodium thiosulphate solution, dried over anhydrous MgSO₄, and recovered to crude product which was purified by silica gel column chromatography (eluent: hexane); yield = 5.24 g, 92 %. ¹H NMR (500 MHz, CDCl₃) δ = 8.31 (d, *J* = 1.6 Hz, 2H), 7.70 (dd, *J* = 8.6, 1.7 Hz, 2H), 7.16 (dd, *J* = 8.5, 3.2 Hz, 2H), 4.20 (t, *J* = 7.2 Hz, 2H), 1.87–1.75 (m, 2H), 1.41–1.16 (m, 10H), 0.85 (t, *J* = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ = 139.62, 134.26, 129.79, 124.00, 110.92, 81.66, 43.57, 31.89, 29.33, 29.15, 28.84, 27.24, 22.61, 14.09.

2.2.3. 9-Octyl-3,6-bis((trimethylsilyl)ethynyl)-9H-carbazole (3)

A mixture of dry THF and triethylamine (30 mL; 1: 1) was degassed for 1 h, and compound **2** (2 g, 3.76 mmol) and copper iodide (35 mg, 0.18 mmol) were added. To the resulting reaction mixture, trimethylsilylacetylene (TMSA) (2.61 mL, 18.8 mmol) and catalytic amount of bis(triphenylphosphine)palladium(II) dichloride (5% mol) were added, and the reaction was stirred at room temperature for 48h. The reaction mixture was filtered through Celite, concentrated under vacuum, and the crude product was dissolved in dichloromethane and washed with water (× 3) followed by brine. The organic layer was dried over anhydrous MgSO₄ and recovered to get crude brown liquid which was purified by silica gel column chromatography (eluent: hexane) to afford compound **3** as a yellow viscous oil; yield = 1.58 g, 89 %. ¹H NMR (500 MHz, CDCl₃) δ = 8.19 (d, *J* = 1.1 Hz, 2H), 7.58–7.55 (dd, *J* = 1.6 Hz, *J* = 1.5 Hz, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 4.24 (t, *J* = 7.2 Hz, 2H), 1.84–1.80 (m, 2H), 1.31–1.26 (m, 10H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.29 (s, 18H); ¹³C NMR (100 MHz, CDCl₃) δ = 140.37, 129.82, 124.54, 122.15, 113.65, 108.64, 106.22, 92.04, 43.07, 31.59, 29.15, 29.00, 28.76, 27.08, 22.44, 20.13, 13.91; ESI-MS (m/z) [M+Na]⁺: 495.

2.2.4. 3,6-Diethynyl-9-octyl-9H-carbazole (4)

Compound **3** (1.5 g, 3.17 mmol) was dissolved in a solvent mixture of MeOH: THF (ν/ν , 1:1) and finely powdered K₂CO₃ (2.19 g, 15.8 mmol) was added. The reaction mixture was stirred at room temperature for 5 hr and the solvent was evaporated under reduced pressure. The crude solid was dissolved in diethyl ether and washed with water followed by brine. The organic layer was evaporated and the crude mass was subjected to column chromatography on silica (eluent: hexane) to afford **4** as a light-yellow solid; yield = 0.95 g, 92 %. ¹H NMR (500 MHz, CDCl₃) δ = 8.22 (d, *J* = 1.1 Hz, 2H), 7.60 (dd, *J* = 8.5, 1.5 Hz, 2H), 7.34 (d, *J* = 8.5 Hz, 2H), 4.27 (t, *J* = 7.3 Hz, 2H), 3.08 (s, 2H), 1.88–1.80 (m, 2H), 1.58 (s, 2H), 1.38–1.18 (m, 10H), 0.86 (t, J = 7.0 Hz, 3H); ¹³C NMR (125 MHz, CDCl₃) δ = 140.69, 130.15, 124.79, 122.28, 112.71, 108.97, 84.76, 75.46, 43.37, 31.77, 29.32, 29.15, 28.94, 27.25, 22.61, 14.07; ESI-MS (m/z) [M+H]⁺: 328 (30%) and [M+NH4]⁺: 346 (100%).

2.2.5. 7,7'-(((9-Octyl-9H-carbazole-3,6-diyl)bis(ethyne-2,1-diyl))bis(4,1-phenylene))bis(2hexadec ylbenzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone) (**NDICz-4**)

Compounds **4** (0.3 g, 0.91 mmol) and **5** (1.3 g, 1.9 mmol) were dissolved in a solvent mixture of dry THF: *N*,*N*-diisopropylethylamine (DIPEA) (30 mL; 1: 1) and the resulting solution was degassed using nitrogen gas. Copper iodide (87 mg, 0.045 mmol) and tetrakis(triphenylphosphine)palladium(0) (52 mg, 5 mol%) were added to the reaction mixture. The resulting suspension was refluxed for 24 h. The completion of the reaction was monitored by thin layer chromatography and was worked-up using the same procedure reported for compound 3 to afford **NDICz-4** as a light brown solid (column in DCM: hexane 70: 30); yield = 0.93 g, 70 %. FT-IR (KBr, cm⁻¹): 3421, 3081, 2921, 2850, 2208, 1709, 1664,

1580, 1509, 1451, 1342, 1243, 1186, 766; ¹H NMR (400 MHz, CDCl₃) δ = 8.83–8.77 (m, 8H), 8.30 (d, J = 1.2 Hz, 2H), 7.80–7.74 (m, 4H), 7.69 (dd, J = 8.5, 1.5 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 7.37–7.32 (m, 4H), 4.31 (t, J = 7.2 Hz, 2H), 4.25–4.18 (m, 4H), 1.94–1.86 (m, 2H), 1.82–1.71 (m, 4H), 1.49–1.23 (m, 62H), 0.88 (t, J = 6.9 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 162.90, 162.73, 140.48, 133.87, 132.57, 131.37, 130.96, 129.84, 128.66, 126.96, 126.79, 126.57, 125.00, 124.25, 122.39, 113.69, 109.06, 91.85, 87.24, 77.36, 77.04, 76.73, 41.11, 31.95, 31.79, 29.73, 29.58, 29.38, 29.19, 28.99, 28.13, 27.30, 27.14, 22.72, 22.63, 14.15, 14.10; MALDI-TOF: calculated for C₉₆H₁₀₅N₅O₈ [M]⁺ (m/z) 1456.89; found = 1456.95. Elemental analysis calculated for C₉₆H₁₀₅N₅O₈ (%): C 79.14; H 7.26; N 4.81; O 8.79; found C 79.10; H 7.23; N 4.78; O 8.75.

2.2.6.2-(4-(7-Hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-yl)phenyl)-3-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]phenanthrolin-2(1H)-yl)phenyl)ethynyl)-9-octyl-9H-carbazol-3-

yl)buta-1,3-diene-1,1,4,4-tetracarbonitrile (**NDICz-5**)

To a solution of **NDICz-4** (100 mg, 0.068 mmol) in dry THF (5 mL) was added TCNE (87 mg, 0.68 mmol) and the resulting solution was refluxed for 12 h. The progress of reaction was monitored by TLC. After completion of reaction the solvent was evaporated off and the resulting dark brown mass was purified by column chromatography (silica gel; hexane: DCM 1: 9) to afford titled **NDICz-5** as a cherry solid (97 mg, 90%); FT-IR (KBr, cm⁻¹): 3449, 2922, 2851, 2222, 1711, 1666, 1582, 1509, 1452, 1337, 1245, 1186, 880, 813, 766; ¹H NMR (500 MHz, CDCl₃) δ = 8.82–8.77 (m, 8H), 8.54 (d, *J* = 2.0 Hz, 1H), 8.37 (d, *J* = 1.0 Hz, 1H), 8.06 (dd, *J* = 8.9, 2.0 Hz, 1H), 8.02–7.96 (m, 2H), 7.80–7.73 (m, 3H), 7.61–7.55 (m, 3H), 7.46 (d, *J* = 8.5 Hz, 1H), 7.38–7.32 (m, 2H), 4.36 (t, *J* = 7.2 Hz, 2H), 4.25–4.16 (m, 4H), 1.93–1.91 (m, 2H), 1.79–1.71 (m, 4H), 1.49–1.20 (m, 62H), 0.89–0.86 (m, 9H); ¹³C NMR

(100 MHz, CDCl₃) δ = 165.74, 162.89, 162.67, 162.49, 144.20,140.88,139.86, 134.18, 132.57, 131.88, 131.62, 131.41, 130.99, 130.62, 130.41, 128.69, 127.64, 127.21, 127.01, 126.49, 126.03, 124.75, 124.40, 123.82, 123.47, 122.39, 121.76, 115.78, 113.09, 112.20, 111.60, 111.15, 110.68, 109.92, 90.80, 88.27, 81.93, 88.21, 81.51, 43.87, 41.07, 31.99, 31.71, 29.65, 29.51, 29.32, 29.07, 28.97, 28.06, 27.20, 27.07, 22.66, 22.55, 14.09, 14.03; MALDI-TOF: calculated for C₁₀₂H₁₀₅N₉O₈ [M]⁺ (m/z) 1584.98; found = 1584.16; [M+H]⁺ = 1586.15; [M+2H]⁺ = 1587.20. Elemental analysis calculated for C₁₀₂H₁₀₅N₉O₈ (%): C 77.29; H 6.68; N 7.95; O 8.08; found C 77.24; H 6.64; N 7.92; O 8.03.

2.2.7. 2-(4-(3,3-Dicyano-2-(4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo[lmn][3,8]ph enanthrolin-2(1H)-yl)phenyl)-1-(6-((4-(7-hexadecyl-1,3,6,8-tetraoxo-3,6,7,8-tetrahydrobenzo [lmn][3,8]phenanthrolin-2(1H)-yl)phenyl)ethynyl)-9-octyl-9H-carbazol-3-yl)allylidene)cyclohex a-2,5-dien-1-ylidene)malononitrile (**NDICz-6**)

Compounds **NDICz-4** (100 mg, 0.068 mmol) and TCNQ (139 mg, 0.68 mmol) were suspended in 1,2- dichlorobenzene and the resulting reaction mixture was stirred at 120 °C. The progress of reaction was monitored by TLC. The solvent was evaporated under reduced pressure and the crude residue was purified by column chromatography (silica gel; eluent: DCM) to afford **NDICz-6** as a bluish-black solid (82 mg, 72%); FT-IR (KBr, cm⁻¹): 3448, 2921, 2850, 2209, 1710, 1669, 1582, 1452, 1339, 1245, 1190, 766; ¹H NMR (400 MHz, CDCl₃) δ = 8.78 (dd, *J* = 18.6, 7.3 Hz, 8H), 8.35 (s, 1H), 8.10 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.74 (t, *J* = 7.4 Hz, 3H), 7.58 (dd, *J* = 9.6, 1.9 Hz, 1H), 7.53–7.42 (m, 5H), 7.41–7.32 (m, 4H), 7.21 (dd, *J* = 9.6, 1.9 Hz, 1H), 4.34 (t, 2H), 4.20 (dd, *J* = 17.2, 9.6 Hz, 4H), 1.91 (d, *J* = 7.3 Hz, 2H), 1.82–1.68 (m, 4H), 1.49–1.19 (m, 62H), 0.87 (td, *J* = 6.8, 3.0 Hz, 9H); ¹³C NMR (100 MHz, CDCl₃) δ = 170.24, 162.90, 162.69, 162.53, 162.48, 153.83, 150.92, 142.60, 140.84, 139.17, 135.75, 134.31, 134.06, 133.84, 132.52, 131.59, 131.42, 130.99,

130.83, 130.59, 130.34, 129.63, 128.67, 127.25, 127.04, 126.81, 126.51, 125.99, 124.57, 123.70, 122.38, 115.01, 114.03, 113.74, 113.69, 112.54, 112.22, 110.30, 109.67, 91.19, 88.25, 87.88, 84.78, 43.73, 41.30, 31.94, 31.90, 31.74, 29.67, 29.33, 29.12, 29.01, 28.07, 27.26, 27.08, 22.67, 14.093; MALDI-TOF: calculated for $C_{108}H_{109}N_9O_8$ [M]⁺ (m/z) 1661.08; found = 1661.93, [M+H]⁺ = 1662.95. Elemental analysis calculated for $C_{108}H_{109}N_9O_8$ (%): C 78.09; H 6.61; N 7.59; O 7.71; found C 78.05; H 6.57; N 7.53; O 7.69.

3. Results and discussion

3.1. Design and synthetic strategies

We designed these novel molecules to be V-shaped, and by combining electron rich and electron poor subunits, such as Cz and NDI, respectively, presuming it might help to improve charge transfer transition and in turn electron accepting properties. To achieve this, firstly we developed NDICz-4 based on an A-D-A format comprising NDI and Cz functionalities interlinked with acetylenic bond. Then the reaction of NDICz-4 was carried out with TCNE and TCNQ to afford NDICz-5 and NDICz-6, respectively, thus generating A-A₁-D-A format. The successful synthesis of NDICz-4 was carried out using the Sonogashira-Hagihara coupling reaction where intermediates 4 and 5 were reacted using tetrakis (triphenylphosphine)palladium(0) catalyst. The synthesis of intermediates 4 and 5 was carried out using the literature procedures [59]. All of the synthetic details are depicted in Scheme 1. For the synthesis of NDICz-5 and NDICz-6, the [2 + 2] cycloaddition (CA) reaction followed by retro-electrocyclization (RE) reaction of NDICz-4 with TCNE and TCNQ was conducted, respectively, according to the procedure reported in the literature (Scheme 2) [57,58]. This reaction strategy is highly successful due to the simplicity of transformation and generally provides higher yields. For example, NDICz-5 was obtained in 90% yield when the

reaction of NDICz-4 was carried out with TCNE in THF at 66 °C. We observed that only one acetylene subunit in NDICz-4 was reacted with TCNE. To check the reactivity of second acetylene subunit, we performed the reaction of NDICz-5 with TCNE in THF at 80 °C in a sealed tube for 2 days. No transformation was observed from NDICz-5 to NDICz-7 (Scheme 3), thus implying that Cz subunit of NDICz-5 experiences electron deficiency which in turn stops a further [2 + 2] CA-RE reaction with TCNE. This suggests that it is important to balance the donor-acceptor subunits to proceed a further [2 + 2] CA-RE reaction. As we successfully synthesized **NDICz-5** using THF as the reaction solvent, we thought to employ the same reaction conditions to generate NDICz-6. But surprisingly, the reaction didn't occur in the presence of THF, thus, prompting us to evaluate the effect of solvent and temperature on the reactivity of NDICz-4 towards TCNQ. Dichlorobenzene was found to be the most suitable solvent. The [2 + 2] CA-RE reaction of NDICz-4 with TCNQ was conducted in dichlorobenzene at 120 °C for 24 h affording NDICz-6 as a dark green solid in 72% yield (Scheme 2). An effort to react NDICz-6 with an excess of TCNQ in dichlorobenzene at 140 °C for 3 days did not yield NDICz-8 (Scheme 3). Thus, we realized that not only the donoracceptor subunits, but the TCNQ moiety renders the reduction of alkyne reactivity.

> Scheme 3

3.2. Thermal properties

The thermogravimetric and differential scanning calorimetry (DSC) analyses were carried out to investigate thermal properties of NDICz-4, NDICz-5 and NDICz-6. Under nitrogen atmosphere, the thermogravimetric analysis (TGA) of all the three compounds NDICz-4, NDICz-5 and NDICz-6 experienced 5% weight loss at 426 °C, 460 °C and 375 °C, respectively, suggesting that the materials are thermally stable (Figures S1, S2 and S3 in

Supporting Information (SI)). The DSC traces of **NDICz-4** and **NDICz-5** are shown in Figures S4 and S5 (SI), respectively, suggesting the melting point temperatures of 221.72 °C and 184.95 °C. On the other hand, **NDICz-6** demonstrated crystalline behavior at 261.54 °C, thus, indicating that it exhibits stronger intermolecular interactions in its solid state (Fig. S6; SI). These analyses revealed these materials to be thermally stable, meaning that the BHJ devices can be annealed at a higher temperature, e.g. > 100 °C), if required.

3.3. Photophysical properties

The optical absorption spectra of NDICz-4, NDICz-5 and NDICz-6 in chloroform solution and as a thin solid film are shown in Fig. 2. NDICz-4 showed absorption peaks at 314 nm and 344 nm (shoulder peak) with two major peaks at 360 nm and 380 nm. NDICz-5 displayed absorption peaks at 344 nm (shoulder peak), 360 nm, 380 nm and one broad peak at 475 nm. NDICz-6 bearing TCNQ functionality exhibited absorption peaks at 344 nm (shoulder peak), two major peaks at 360 nm and 380 nm and two broad peaks at 450 nm and 600 nm. The absorption peaks of NDICz-4, NDICz-5 and NDICz-6 appeared at ~400 nm can be assigned to $\pi \to \pi^*$ transitions (S0 \to S2) of the NDI moieties. The peaks for NDICz-5 appeared at 475 nm, and for NDICz-6 at 450 nm and 600 nm can be ascribed to strong intramolecular charge transfer (ICT) transitions from the donor Cz subunit to the acceptor NDI and the additional A₁ moieties. The absorption peaks for NDICz-4 in thin film form exhibited peaks at 315 nm and 357 nm, whereas for NDICz-5, the peaks appeared as one shoulder peak at 304 nm and two prominent peaks at 361 nm and 383 nm together with a broad peak at 463 nm. As a thin film, NDICz-6 exhibited peaks at 319 nm (shoulder peak), two peaks at 363 nm and 383 nm, and a broad peak at 600 nm. The broad absorption maxima at 463 nm and 600 nm suggest that thin films of NDICz-5 and NDICz-6 possess effective π - π stacking in their solid state and have an ability to exhibit superior light-harvesting

properties when compared with their structural analogue **NDICz-4**. These results clearly indicate that incorporation of additional acceptor units, TCNE and TCNQ, can indeed be utilized for absorbing a larger amount of the solar spectrum.

>Fig. 2<

The estimated optical band gaps of NDICz-4, NDICz-5 and NDICz-6 using the onset of film absorption were 3.02 eV, 2.13 eV and 1.59 eV, respectively, and are depicted in Table S1 (ESI). The optical band gaps of NDICz-5 and NDICz-6 are narrower than that of NDICz-4, suggesting their strong electron accepting capacity due to the incorporation of TCNE and TCNQ functionalities that connect the Cz and NDI subunits of the molecular backbone. Thus, our molecular design strategy can be useful for controlling the absorption properties together with manipulating energy levels and plausibly increasing photovoltaics performance. The normalized absorption spectra of the blends of NDICz-4, NDICz-5 and NDICz-6 with P3HT (D: A 1: 1.5) are given in Fig. 3. According to the blend film spectra shown in Fig. 3, it is apparent that the blend films have more favorable optical absorption throughout the entire visible region. Therefore, the use of a commercially available donor polymer, such as P3HT, is indeed helpful to carry out OPV study and to observe initial performance. We also investigated the steady state emission properties of NDICz-4, NDICz-5 and NDICz-6 in their chloroform solutions. The emission spectra are shown in Fig. S7, SI.

>Fig. 3<

3.4. Computational Calculations

The geometrical optimization of NDICz-4, NDICz-5 and NDICz-6 with truncated alkyl chains was performed at the B3LYP/6-31G(d) level of theory using the Gaussian 09 ab initio/DFT quantum chemical simulation package [60]. The frequency calculations were carried out to ensure the structures of molecule to be real. The obtained geometries of NDICz-4, NDICz-5 and NDICz-6 at the B3LYP/6-31G(d) level were subjected to the timedependent density functional theory (TD-DFT) studies using M062X/6-31G(d) [61]. The frontier molecular orbitals (FMOs) calculated at the M062X/6-31G(d) level of theory and generated using Avogadro are given in Fig. 4 and Fig. S8, SI [62]. In case of NDICz-4, the HOMO electron density resided over Cz and acetylene-linked phenyl subunits, whereas the LUMO was localized over the terminal NDI unit. The former was true for both NDICz-5 and NDICz-6, given the donating strength of Cz functionality. The LUMO density for NDICz-5 was mainly residing on terminal NDI unit, but for NDICz-6, there was a strong contribution from the TCNQ functionality. This is logical given the accepting strength of TCNQ and its role in tuning the energy levels, though the levels L+1 and L+2 inhabited on NDI unit. Overall, there was a good segregation between the HOMO and the LUMO densities, thus, generating an ideal environment for the ICT transition over the whole molecular backbone. The obtained TD-DFT results at the M062X/6-31G(d) level of theory for NDICz-4, NDICz-5 and NDICz-6 are depicted in Table S2 (SI). The computed absorption spectra shown in Figures S9, S10 and S11 (SI) indicated transition peaks which are mainly described as the HOMO \rightarrow LUMO transition. Moreover, the enhancement of ICT transition in NDICz-6 followed by NDICz-5 and NDICz-4 was further confirmed by evaluating the dipole moment values using the M062X/6-31G(d) level of theory (see Table S3; SI).

>Fig. 4<

3.5. Energy levels and electrochemical investigation

As such, the experimental estimation of the HOMO energies was carried out using photo electron spectroscopy in air (PESA) and the LUMO energies were calculated by adding the optical band gap (film spectra) to the HOMO values (for PESA curves see Fig. S12 SI). The LUMO levels of NDICz-5 and NDICz-6 were deepest when compared with the LUMO level of NDICz-4. This suggests the influence of strong accepting functionality, of which TCNQ in NDICz-6 is an example, in tuning the overall energy levels. A similar drop of the LUMOs was also observed while conducting DFT calculations (Theoretical LUMOs of NDICz-4, NDICz-5 and NDICz-6 were 2.63 eV, 2.71 eV and 3.20 eV, respectively), a result that provides a good support to our experimental findings. These theoretical and experimental findings strongly indicate that the A-A₁-D-A format really plays a crucial role for density segregation, efficient light-harvesting, and tuning optical energy levels when compared with the A-D-A format. The electrochemistry experiments revealed that the investigated materials undergo reversible reduction cycles, thus suggesting their suitability as *n*-type materials in BHJ devices (for cyclic voltammograms, see Fig. S13; SI). The HOMO and the LUMO energy levels of NDICz-4, NDICz-5 and NDICz-6 were estimated from the onsets of the oxidation and reduction potentials (Table S1), respectively, including the standard value of ferrocene to be -4.8 eV. It was observed that the energy levels deduced from the cyclic voltammetry experiments were found to follow a similar pattern as was determined using PESA.

3.6. Photovoltaic properties

The photovoltaic performance of NDICz-4, NDICz-5 and NDICz-6 was investigated by fabricating solution-processable BHJ devices using the conventional and simple configuration ITO/PEDOT: PSS/active layer/PFN/Al and with P3HT as a donor. We also fabricated P3HT: PC₇₁BM devices so as to realize the validity of our testing strategy. The performance of BHJ devices was optimized by adjusting the blend ratio of donor to acceptor and by solvent vapor annealing (SVA) technique. It was found that the donor to acceptor weight ratio of 1: 1.5, respectively, was crucial for optimum performance. The devices incorporating NDICz-4, NDICz-5 and NDICz-6 as non-fullerene acceptors yielded moderate outcome and the efficiency numbers reached 2.32 % 1.82 % and 3.83 %, respectively. However, we preceded the SVA treatment of active layers in order to observe an improvement of bulk film morphology and hence, device performance. We used carbon disulfide vapors for SVA treatment before the deposition of PFN/Al cathode layer. After SVA treatment, we undoubtedly observed a notable change in the blend film morphology that, as per the literature and our own understanding, led to an improved device performance. That being said, we conducted atomic force microscopy (AFM) analysis of the pre- and postannealed blend surfaces. The AFM analysis clearly indicated that the post-annealed blend surfaces show lesser roughness, well-plaited donor and acceptor domains and phaseseparated nanoscale morphology. The annealed blend surfaces showed surface roughness of 1.98 nm (P3HT: NDICz-4), 2.12 nm (P3HT: NDICz-5) and 1.71 nm (P3HT: NDICz-6), thereby suggesting that all of the newly developed non-fullerene acceptors are highly miscible with their donor counterpart i.e. P3HT. After the optimization of solvent annealing time (40 seconds), P3HT: NDICz-4 (1: 1.5), P3HT: NDICz-5 (1:1.5) and P3HT: NDICz-6 (1:1.5) blends showed overall PCE of 3.94 %, 4.94 % and 7.58 %, respectively. It is apparent that the superior morphological properties of NDICz-6-based blend have had a greater effect on efficiency when compared with NDICz-4 and NDICz-5-based blends. In contrast, the

maximum PCE reached 3.08% for a controlled device based on P3HT: PC₇₁BM. For current–voltage (*J*–*V*) curves and detailed device parameters, see Fig. 5 and Table 1, respectively. The actual surface morphologies of the blend films of NDICz-4, NDICz-5 and NDICz-6 (1: 1.5 w/w) are shown in Fig. 6. Fig. S14 (SI) represents the distribution of cell parameters for the champion cell based on P3HT and NDICz-6 (P3HT: NDICz-6 (1: 1.5); SVA-treated films).

>Fig. 5<

>Table 1<

Not only did we physically observe the smoothness of blend films, which were free from perceptible projections, lumps and indentations, but also discern that there may be a structural reorganization in the active layer (based on AFM analysis) after SVA treatment. The SVA treated active layers were preceded for optical absorption analysis. The optical absorption spectra not only revealed the broadening of the shoulder peak but were slightly red-shifted when compared with the pre-treated blends (Fig. 7). Both features were prominent in case of **NDICz-6**-based blend when compared with **NDICz-4** and **NDICz-5**-based blends. The slight red-shift and the broadness of spectra do point out a structural rearrangement and hence, improved device performance where the improvement is mainly due to an increase in the short-circuit current density. Furthermore, to examine the well intermixing of donor and acceptor domains, we conducted transmission electron microscopy (TEM) analysis. The TEM analysis did indicate fine, flat textures for all the blends (see Fig. S15, SI), albeit the appearance and fineness of P3HT: **NDICz-6** lie 1.5; pre- and post-SVA treated) suggested that the post-SVA treated surface is a surface which indicates some sort of

crystallinity – a result corroborating AFM analysis – when compared with the unannealed blend surface (Fig. S16, SI). Not only did the image indicate a surface with more desirable morphology (post-SVA treated), but advocate that such regularized blend surfaces usually result in relatively higher values of J_{sc} and FF, as is the case of **NDICz-6** blend. Furthermore, we conducted the wide-angle X-ray diffraction (WAXRD) analysis in order to observe any surface crystallinity in the annealed blend. The presence of peaks in **NDICz-6**-based annealed blend does suggest some sort of crystallinity, a result that corroborates with AFM and TEM analysis, when compared with the unannealed blend surface (for WAXRD spectra, see Fig. S17, SI). This further validates the improved performance of annealed blend surfaces and suggests that the SVA treatment is helpful for the investigated class of V-shaped, nonfullerene electron acceptors to achieve higher device outcomes.

>Fig. 6<

>Fig. 7<

The devices based on NDICz-4 and NDICz-5 showed the highest and the lowest values of V_{oc} , respectively, which in fact is in agreement with the LUMO values of these acceptors, given the V_{oc} is directly proportional to the energy difference between the HOMO of donor and the LUMO of acceptor. The difference for P3HT: NDICz-4 is 1.74 eV, whereas for P3HT: NDICz-5, it is 1.08 eV. The value of J_{sc} is highest for P3HT: NDICz-6 (11.64 mA/cm²) and lowest for P3HT: NDICz-4 (6.16 mA/cm²). The latter value may be attributed to the insufficient driving force (0.26 eV) for exciton dissociation for P3HT: NDICz-4 active layer, since the driving force for exciton dissociation is related with the energy difference between the LUMOs of donor and acceptor employed in the active layer which should be higher than the exciton binding energy (~0.3–0.5 eV). This driving force for P3HT: NDICz-5

and P3HT: **NDICz-6** is about 0.97 eV and 0.73 eV, respectively, and is larger than the threshold driving force, leading to the higher values of J_{sc} when compared with **NDICz-4**-based devices.

To ascertain the accuracy of *J-V* measurements, incident photon to current conversion efficiencies (IPCEs) were measured and are shown in Fig. 5b. The devices based on P3HT: **NDICz-4** and P3HT: **NDICz-5** displayed IPCE spectra up to 600 nm with two bands, i.e. in shorter (300–400 nm) and longer (400–600 nm) wavelength regions, corresponding to the photocurrent generation due to the absorption of photons by non-fullerene acceptor and P3HT, respectively. It can be seen from Fig. 5b that the devices based on P3HT: **NDICz-5** showed higher IPCE and broader response when compared with the devices based on P3HT: **NDICz-4**. This may be attributed to the broader absorption of **NDICz-5**, thereby contributing to an efficient exciton generation and producing more photocurrent. In case of P3HT: **NDICz-6**, the IPCE spectrum is much broader together with higher value when compared with other two combinations. The J_{sc} values calculated by integrating the IPCE data with the AM 1.5G solar spectrum are 6.84 mA/cm², 11.41 mA/cm² and 13.52 mA/cm² for the devices based on P3HT: **NDICz-4**, P3HT: **NDICz-5** and P3HT: **NDICz-6**, respectively, which agree with the values obtained from *J–V* measurements.

In order to get information about photoinduced charge transfer in active layers, we also measured the photoluminescence (PL) spectra of pristine P3HT and blended films as shown in Fig. S18 (SI; excitation wavelength = 520 nm). The pristine P3HT film displayed a strong emission peak at 656 nm which was quenched after mixing with the investigated acceptors. The PL quenching was 70%, 87% and 92% for NDICz-4, NDICz-5 and NDICz-6, respectively. These values follow the J_{sc} and device performance trends. The lowest value of

PL quenching for the P3HT: **NDICz-4** blend may be related to the efficient driving force for this active layer as the LUMO offset is below the threshold value for the exciton dissociation.

To obtain information about the difference in the performance of BHJ devices employing these non-fullerene acceptors, the relationship between photocurrent (J_{ph}) and effective voltage (V_{eff}) was investigated and is reported in Fig. 8 [63]. The J_{ph} value is defined as the difference between $J_{\rm L}$ and $J_{\rm D}$, where $J_{\rm L}$ and $J_{\rm D}$ are the current densities under illumination and dark, respectively. The $V_{\rm eff}$ is estimated from the difference between $V_{\rm a}$ and $V_{\rm o}$ where $V_{\rm a}$ is the applied voltage and V_0 is the voltage at which J_{ph} is zero. At low V_{eff} , the J_{ph} for devices based on P3HT: NDICz-5 and P3HT: NDICz-6 increase dramatically and reaches a plateau at high voltage and is subsequently saturated, thus suggesting that free carriers are swept out efficiently. In comparison, the J_{ph} of devices based on P3HT: NDICz-4 active layer increases at a slower rate and is saturated at a high V_{eff} value, which indicates less efficient charge carrier extraction. This also indicates that the $V_{\rm eff}$ is not high enough to sweep out all the charge carriers from active layer to the electrodes. Moreover, the saturation photocurrent (J_{phsat}) of P3HT: NDICz-4 devices is lower than the J_{phsat} of devices based on P3HT: NDICz-5 and P3HT: NDICz-6 combinations. The higher J_{phsat} suggests that the charge carrier generation in the SVA-treated devices is more efficient than the as-cast devices, which in fact is consistent with their correspondingly higher J_{sc} values. These observations can be ascribed to the lower charge recombination after SVA treatment. The exciton dissociation (η_{diss}) and charge collection (η_{coll}) efficiencies were estimated from the expressions J_{ph}/J_{phsat} at short circuit and $J_{\rm ph}/J_{\rm phsat}$ at maximum power point, respectively. The $\eta_{\rm diss}/\eta_{\rm coll}$ values were 0.78/0.67, 0.89/0.76 and 0.92/0.78 for the devices based on P3HT: NDICz-4, P3HT: NDICz-5 and P3HT: NDICz-6, respectively. The higher values of both the η_{diss} and η_{coll} for the devices based on NDICz-5 and NDICz-6 indicate that exciton dissociation and charge

collection is more efficient in these solar cells when compared with the devices based on P3HT: **NDICz-4** combination. In general, at high value of V_{eff} , the η_{diss} and η_{coll} efficiencies approach to unity, the J_{phsat} mainly depends on the exciton generation rate (G_{max}) and is expressed as $J_{\text{phsat}} = \text{qL}G_{\text{max}}$, where q is the elementary charge and L is the thickness of the active layer. The G_{max} was calculated to be $0.62 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{phsat}} = 8.92 \text{ mA/cm}^2$), $0.82 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{phsat}} = 12.65 \text{ mA/cm}^2$) and $1.02 \times 10^{28} \text{ m}^{-3} \text{ s}^{-1}$ ($J_{\text{phsat}} = 14.70 \text{ mA/cm}^2$) for the devices based on **ND1Cz-4**, **NDICz-5** and **NDICz-6**, respectively. The enhanced value of G_{max} suggests that more excitons are generated in the blend film of **NDICz-6**, a result that is consistent with the higher performance of P3HT: **NDICz-6** when compared with other two combinations.

> Fig. 8 <

To gain an insight into the effective charge carrier mobilities, the space charge limited current (SCLC) method was applied to get information about the charge transportation in the devices. The electron-only devices, consisting of active layer sandwiched between a ZnO coated ITO electrode and LiF/Al counter-electrode as the hole-blocking contact, were fabricated as per the sketch depicted in Fig. S19, SI. We fabricated these devices using **NDICz-5** and **NDICz-6** as only these materials gave reasonable OPV performance. From the current density as a function of voltage data (Fig. S19, SI), the electron mobility in the trap-free SCLC region can be estimated using the Mott-Gurney equation, $[(J = 9 (\epsilon \mu)/8 \times (V^2/d^3); where \epsilon is the dielectric constant, <math>\mu$ is the charge-carrier mobility, d is the sample thickness, and V is the applied voltage]. Using this expression, the electron mobilities of the order of 10^{-4} cm²/Vs and 10^{-3} cm²/Vs were observed for **NDICz-5** and **NDICz-6**, respectively. It is vital to mention that the mobilities of the obtained order, and P3HT: **NDICz-6** in particular, are well within the mobility range exhibited by $PC_{71}BM$ (typically ranging $10^{-3}-10^{-4}$ cm² V⁻¹ s⁻¹), and are an indication of good device performance. Evidently, the observance of good electron mobilities further supports the design principle of these new materials.

4. Conclusions

We have been able to demonstrate the successful use of an A-A₁-D-A type modular format in BHJ solar cells. The new materials **NDICz-5** and **NDICz-6** were designed and synthesized based on the A-A₁-D-A format and their optoelectronic and photovoltaic properties were directly compared with a structural analogue **NDICz-4**, which was based on a simple A-D-A modular design. All the materials were designed to be V-shaped. It was observed that **NDICz-5** and **NDICz-6** exhibited superior properties, such as light-harvesting, enhanced photocurrent density and overall device performance, when compared with **NDICz-4**. Overall, **NDICz-6** performed better than any of the three materials reported herein. It is notable to mention that not only are **NDICz-4**, **NDICz-5** and **NDICz-6** the first examples in the literature which comprise promising building blocks, such as carbazole and naphthalene diimide, but the device parameters outlined herein are among the highest numbers reported in this class of materials.

Acknowledgements

S.V.B. (IICT) is grateful for the financial support from SERB, SB/S1/IC-009/2014, New Delhi, India [IICT Communication Number IICT/Pubs./2018/178]. S.V.B. (GU) acknowledges University Grant Commission (UGC) – Faculty Research Program (India) – for providing financial support and an award of professorship. P.S.R. acknowledges SRF fellowship from CSIR, New Delhi. A.L.P acknowledges the use of the Gaussian 09 procured under the DST-FIST Scheme (Sanction No. FS/FST/PSI-018/2009). R.S.B. acknowledges

financial support from the CSIR, New Delhi under the SRA scheme [13(8772)-A)/2015-Pool]. J. Li acknowledges the Australian Research Council (ARC) for support through a Future Fellowship project (FT130100057). The CSIRO Division of Manufacturing, Clayton Victoria, Australia is acknowledged for providing support through a visiting fellow position for A. G. A. G. acknowledges a vast variety of facilities at Deakin University, RMIT University and Bio 21 Institute, the University of Melbourne, Melbourne, Victoria Australia.

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Captions

Fig. 1. Molecular structures of newly designed and synthesized non-fullerene electron acceptors, NDICz-4, NDICz-5 and NDICz-6.

Scheme 1. Synthetic protocol adopted to synthesize NDICz-4. Reagents and conditions: i) NaH, Dry DMF, overnight reflux; ii) NIS, CHCl₃: CH₃COOH (ν/ν , 1: 1), room temperature (dark); iii) trimethylsilylacetylene (TMSA), Pd(PPh₃)₂Cl₂/CuI, dry THF: triethylamine (1: 1), room temperature; iv) K₂CO₃, MeOH: THF (ν/ν , 1:1), room temperature; v) Pd(PPh₃)₄/CuI, dry THF: *N*,*N*-diisopropylethylamine (DIPEA) (1: 1), 24 h reflux.

Scheme 2. Synthesis of compounds NDICz-5 and NDICz-6.

Scheme 3. Attempted, and unsuccessful, synthetic trials to afford NDICz-7 and NDICz-8.

Fig. 2. Absorption spectra of compounds **NDICz-4**, **NDICz-5** and **NDICz-6** in their chloroform solutions and in thin solid films.

Fig. 3. The UV-Vis absorption spectra of **NDICz-4**, **NDICz-5** and **NDICz-6** as a blend film with P3HT [D: A 1: 1.5 (w/w)].

Fig. 4. Theoretical density distribution for the HOMOs (below) and the LUMOs (up) of NDICz-4, NDICz-5 and NDICz-6.

Fig. 5. (a) Characteristic current-density *vs* voltage (*J-V*) curves for the best BHJ devices based on **NDICz-4/NDICz-5/NDICz-6** in blends with P3HT under simulated sunlight (100 mW cm⁻² AM1.5G); (b) IPCE spectra of the best performing devices described in Fig. 5a.

Fig. 6. AFM images of P3HT: **NDICz-4** [images a (pre-SVA treated and b (post-SVA treated)], P3HT: **NDICz-5** [images c (pre-SVA treated and d (post-SVA treated)], and P3HT: **NDICz-6** [images e (pre-SVA treated and f (post-SVA treated)] blends spin-cast from chloroform solutions at 2500 rpm atop annealed ITO/PEDOT: PSS substrates; (Scale bar = $0.2 \mu m$).

Fig. 7. The optical absorption spectra of pre- and post-SVA treated blend films (D: A 1: 1.5 (w/w)).

Fig. 8. Variation of photocurrent (J_{ph}) with effective voltage (V_{eff}) for the devices based on SVA treated active layers consisting of NDICz-4, NDICz-5, and NDICz-6 as acceptors and P3HT as donor.

Table 1. Photovoltaic cell parameters for P3HT: NDI-Cz4, NDI-Cz5 and NDI-Cz6 blends.



List of Figures, Schemes and Table

















Fig. 5.



Fig. 6.











Acceptor	$J_{\rm sc}$ (mA/cm ²)	V _{oc} (V)	FF	Best PCE (avg)
				%
NDICz-4 (as cast)	4.35	1.08	0.36	1.69 (1.62) ^b
NDICz-5 (as cast)	7.82	0.78	0.38	2.32 (2.25) ^b
NDICz-6 (as cast)	10.34	0.97	0.38	3.83 (3.74) ^b
NDICz-4 (SVA)	6.96 (6.84) ^a	1.03	0.49	3.51 (3.42) ^b
NDICz-5 (SVA)	11.52 (11.41) ^a	0.74	0.58	4.94 (4.85) ^b
NDICz-6 (SVA)	13.67 (13.52) ^a	0.94	0.59	7.58 (7.49) ^b
PC71BM	8.67	0.56	0.64	3.08 (3.01)

a $J_{\rm sc}$ calculated

b Average of ten devices

Research Highlights

- The first effort to utilize the combination of carbazole (Cz) and naphthalene diimide (NDI) functionalities in conjunction with tetracyanoethylene (TCNE) and tetracyanoquinodimethane (TCNQ) units to generate novel, V-shaped non-fullerene electron acceptors
- Creation of A-A₁-D-A design using Cz and NDI, and TCNE/TCNQ units
- Direct comparison of A-A₁-D-A and A-D-A designs in terms of optoelectronic and photovoltaic properties
- The inclusion of TCNE and TCNQ units was primarily done to induce cross-conjugation within the molecular backbone and hence to improve light-harvesting
- One of the materials (**NDICz-6**) afforded the highest efficiency of 7.58% using the conventional donor polymer (P3HT) after the solvent vapour annealing of active layer