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An efficient non-fullerene acceptor based on central and peripheral naphthalene diimides

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Through the coupling of central and terminal naphthalene diimide functionalities, a unique non-fullerene electron acceptor, coded as N10, was designed, synthesized, characterized and applied in solution-processable bulk-heterojunction devices. The target N10 displayed good solubility, excellent thermal stability and energy levels complementing those of the conventional donor polymer poly(3-hexyl thiophene) (P3HT). An excellent power conversion efficiency of 7.65% was obtained in simple BHJ devices (P3HT: N10 1: 1.2), which is the highest so far for the NDI core-based non-fullerene acceptors.

There is clearly a growing global demand for energy and this demand is driven by increasing population and the increasing standards of living of that population requires. The natural, renewable energy resources, such as water, wind and solar energy, are particularly attractive due to their low carbon emission nature. Of such natural resources, sun light is seen as the prime candidate given its abundance on our planet. The capturing of solar power through inorganic and organic photovoltaic devices is a phenomenon that has been extensively studied for the past three decades. The organic devices in particular are a promising next-generation green energy resource as they offer unique advantages, such as

flexibility, low-cost, light weight and solution processability, over their former counterpart.¹ The development of organic, otherwise termed bulk-heterojunction, solar cells in terms of either materials' design or device fabrication strategies has attracted a vast variety of researchers from around the globe. Such bulk-heterojunction (BHJ) devices recently achieved power conversion efficiencies (PCEs) of over 11% with the conventional fullerene acceptors,² thereby suggesting that the fullerene derivatives, such as [6,6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₁BM) and its C₇₁ analogue (PC₇₁BM), are currently the best possible electron acceptors for organic photovoltaic applications.

Not only are the fullerene derivatives compatible with a number of conventional and conjugated polymeric donors, such as poly(3-hexyl thiophene) (P3HT), they exhibit high solubility and good electron mobility together with an ability to form a favourable nanoscale network with versatile donor components.³ Despite such merits, these fullerene derivatives are afflicted with a number of inherent disadvantages such as limited absorption in the visible region, restricted chemical and energetic tuning *via* structural modification, and greater electron affinity that can result in low open-circuit voltage.⁴ These drawbacks encourage researchers to carry out research in finding new structures that can serve as non-fullerene acceptor (NFA) materials. However, such new compounds not only should retain properties such as strong accepting strength, solubility and thermal stability, but must address the limitations of fullerene acceptors, such as structure flexibility, electronic tunability and visible region absorption.

In regards to the design of NFAs, two types of materials, namely small molecules and polymers, can be developed. However, it is arguable that the development of small molecules provides a number of advantages over the development of their polymeric counterparts. Such benefits can be realised in terms of synthetic ease, purification strategies, and less end-group contamination. Moreover, given the ease of making changes to the structure of small molecules, the parameters such as open circuit voltage can be tuned using a

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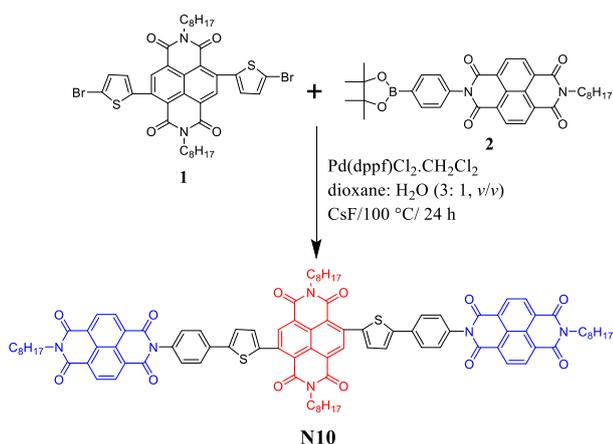
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variety of building blocks, such as donors and acceptors. There are a number of structural types that have been reported in the recent literature where a variety of donor and acceptor units have been combined to generate NFAs.⁵ However, NFAs based on an acceptor–acceptor–acceptor (A–A–A) format, and naphthalene diimide (NDI) core-based in particular, have not been explored to a significant extent, though they are highly promising targets given their strong electron accepting capacity.⁶ The inclusion of NDI functionality in a given target is advantageous in terms of enhancing the solubility of that particular target together with the control of photo-physical properties. Taking into account of the literature precedence, our success with the design and development of NDI core-based NFAs,⁷ and the advantages provided by NDI moiety, herein we report the design, synthesis and characterisation of a novel NFA, **7,7'-((2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthroline-4,9-diyl)bis(thiophene-5,2-diyl))bis(4,1-phenylene))bis(2-octylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone) (N10), where we have used NDI functionalities at the central and peripheral positions (Scheme 1). The design of **N10** gave us a highly conjugated molecule with the presence of a number of alkyl chains (all the chains were considered to be identical (-octyl) from a molecular symmetry point of view) in order to demonstrate excellent film forming capacity without crystallization occurring in the film. Our idea of designing **N10** was validated as the solution-processable BHJ devices based on the blend of P3HT: **N10** (1: 1.2 w/w) afforded PCE as high as 7.65%, a result that is the highest for the NDI core-based NFAs. Moreover, the reported work is the first effort that has been carried out by placing three NDI functionalities in an A–A–A fashion. The present work is a continuation of our research interest in the design and development of small molecule NFAs for organic photovoltaic (OPV) applications.⁸**



Scheme 1 Molecular structure of the newly designed and synthesized NFA **N10** and its synthetic protocol

The newly designed **N10** was synthesized *via* Suzuki coupling reaction between 2-octyl-7-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone and 4,9-bis(5-bromothiophen-2-yl)-2,7-dioctylbenzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-

tetraone. The reaction was conducted in dioxane: water solvent mixture and was run at 100 °C for 24h using cesium fluoride (CsF) as base and [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II), complex with dichloromethane [Pd(dppf)Cl₂·CH₂Cl₂] as the catalyst (Scheme 1). The target **N10** was purified *via* simple column chromatography and its structure was confirmed by ¹H and ¹³C NMR spectroscopies together with MALDI-TOF and elemental analysis (for synthetic details and experimental spectra, see the ESI[†]). **N10** was found to be soluble in a range of common organic solvents, such as chloroform and dichlorobenzene, thus fulfilling one of the major requirements of organic semiconductors to be fabricated in solution-processable OPV devices.

The optical absorption spectra of **N10** were measured in solution, and in pristine and blend films (see Fig. 1). In solution, **N10** exhibited two absorption peaks (362 nm and 382 nm) in the high energy area together with a strong shoulder peak at 543 nm, with the latter being assigned as the absorption maximum (λ_{max}). In the thin solid film state, the absorption peaks were slightly broader and λ_{max} was red-shifted by ~51 nm, suggesting that there exists an effective π - π stacking in the solid state. When **N10** was blended with P3HT, the resultant film displayed strong absorption over most of the visible region, even tailing into the infrared region. This result indicates that there is an efficient charge transfer transition between donor and acceptor components which is usually considered advantageous for improved device outcome.

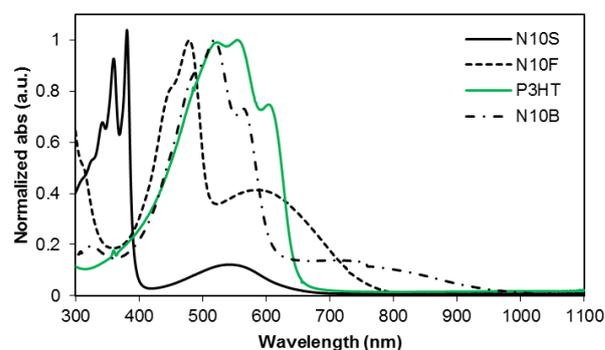


Fig. 1 UV-Vis absorption spectra of **N10** in chloroform solution (**N10 S**), as a pristine film (**N10 F**), and as a blend with P3HT (**N10 B**) [1: 1.2 (w/w)]. The P3HT film absorption spectrum is also shown.

In order to understand the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) densities, we conducted density functional theory (DFT) calculations. The DFT calculations, which were carried out using the Gaussian 09 suite of programs⁹ and the B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory, indicated that the HOMO and the LUMO densities are well separated, with the former lying on the phenyl and thiophene units together with the central NDI functionality and the latter residing on the peripheral NDI units (Fig. S1, ESI[†]). Such separation of theoretical densities is considered ideal for intramolecular charge transfer (ICT) transition and ensures

efficient electron flow upon photo irradiation. Furthermore, the nature of ICT using the time-dependent DFT calculations (TD-DFT) was also elucidated. The TD-DFT calculations were carried out using the optimized ground state geometry of **N10** at the B3LYP/6-311G(d,p) level of theory. The TD-DFT calculations provide excitation energies and oscillator strengths (denoted by f) of the lowest singlet states. The computed absorption spectrum (Fig. S2, ESI[†]) shows the main transition peak at 660.95 nm which is ascribed to HOMO \rightarrow LUMO transition (Excited State 1: 1.8758 eV; 660.95; $f = 0.6234$). Experimentally, the HOMO and the LUMO energy levels were estimated and calculated, respectively, using a combination of photoelectron spectroscopy in air (PESA) and UV-Vis spectroscopy on pristine films. The PESA curve gave an estimated HOMO of -5.70 eV, whereas the LUMO level was calculated to be -4.15 eV, thus providing an optical band gap of 1.55 eV. The energy level diagram depicts these values and indicates that the energy levels are well complementing those of the conventional donor polymer P3HT (for PESA curve and energy level diagram, see Fig. S3 (ESI[†]) and Fig. 2, respectively). We further believed that thermal stability is required of an organic semiconductor to allow a photovoltaic device to survive fabrication and operate in harsh environmental conditions. Therefore, we conducted thermogravimetric and differential scanning calorimetry (DSC) analyses. Both the analyses revealed that **N10** is a thermally stable chromophore which can be processed at high temperature, for instance 100 °C, if required. For TGA and DSC curves, see Fig. S4, ESI[†].

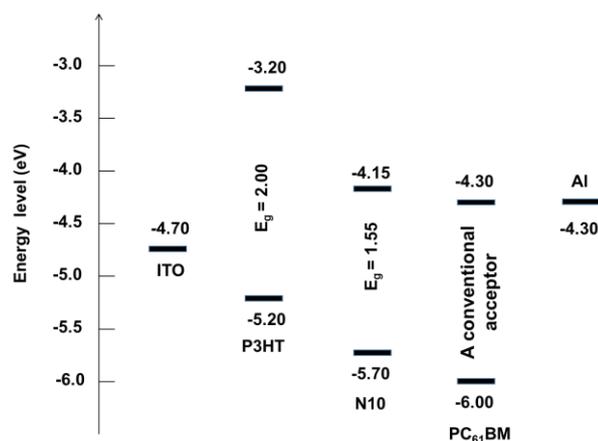


Fig. 2 The energy level diagram showing alignments of different components of a BHJ device architecture

Because of its suitable optoelectronic properties, good film forming capability, solubility, and thermal and chemical stabilities, **N10** was used as an n -type material with the standard donor polymer P3HT as the p -type semiconductor in BHJ devices. We chose a very simple device architecture to start with (ITO/PEDOT: PSS (38 nm)/active layer/Ca (20 nm)/Al (100 nm)), where the active layer was a solution-processed blend of **N10** and P3HT. The active layer was deposited by spin coating the blend solution of **N10** and P3HT in *o*-dichlorobenzene (donor: acceptor 1: 1.2 (w/w)). The optimum layer thickness was

found to be in the range of ~ 70 nm. The choice of a high boiling point solvent, e.g. *o*-dichlorobenzene, was primarily made due to a number of advantages, such as smooth and consistent films avoiding formation of large-scale crystals and easy device processing, it offers.

The annealed blend films that used an optimal ratio of 1: 1.2 (P3HT: **N10**) gave excellent performance and the best photovoltaic cell parameters; V_{oc} , short circuit current density (J_{sc}), fill factor (FF), and PCE, reached 0.99 V, 12.08 mA cm⁻², 0.64, and 7.65%, respectively. The as-cast, unannealed devices afforded reasonable and encouraging photovoltaic performance. A PCE of 4.78% was achieved for unannealed devices. This result is among the highest PCE values that has been attained using the NDI core-based NFAs. It is notable to mention that at this stage we didn't use any barrier or electron transporting layer between Ca electrode and the active layer that is typically used to remove any hole extraction and enhance device performance. The use of such strategies to fabricate devices using **N10** is also underway and the results will be published soon. The standard P3HT:PC₆₁BM device gave 3.03% efficiency when fabricated under similar conditions. The respective current-voltage (J - V) curves for the best devices are represented in Fig. 3, and Table S1 and Fig. S5 (ESI[†]) represent the overall J - V characteristics and a histogram of the device characteristics, respectively.

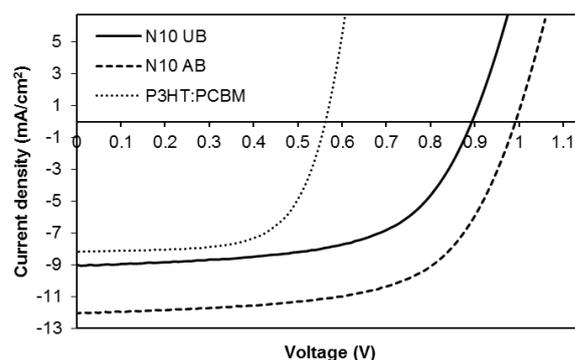


Fig. 3 Characteristic current-density vs. voltage (J - V) curves for the best BHJ devices based on **N10** in blends with P3HT. Solid and dashed lines correspond to pre-annealing (unannealed blend (UB)) and post-annealing (annealed blend (AB)) conditions, respectively, under simulated sunlight (100 mW cm⁻² AM 1.5G), [blend ratio = 1: 1.2 w/w (D/A)]. Device structure was: ITO/PEDOT: PSS (38 nm)/active layer (~ 70 nm)/Ca (20 nm)/Al (100 nm).

The incident photon-to-current conversion efficiency (IPCE) measurement of the active layer indicated a strong and broad response over the entire visible region (350–900 nm), with maximum IPCE $\sim 60\%$ at 618 nm. The broadness of IPCE spectrum indicated a superior blending of donor and acceptor domains, excellent light-harvesting, and that both the components made a considerable contribution to the IPCE and J_{sc} (for IPCE curve, see Fig. S6, ESI[†]). Furthermore, the excellence of the well-knitted blend surface was confirmed by atomic force microscopy (AFM) analysis which was conducted in tapping mode. The AFM analysis revealed a smooth blend surface for unannealed film (surface roughness = 1.2 nm), whereas some grains were observed for the annealed blend surface (surface

roughness = 2.1 nm). Such granular surfaces are considered responsible for providing better, and in fact more desirable, morphology when compared with amorphous and regular morphologies, and are often desired for superior device performance. The superiority of blend surface suggested that **N10** possesses a great ability to be miscible with a variety of donor counterparts, for instance the conventional donor polymer P3HT.

We further carried out transmission electron microscopy (TEM) analysis where a well-interweaved blend surface was noticed, a result that corroborates higher device outcome and AFM analysis (for AFM and TEM curves, see Fig. 4). It is notable to mention that the well intermixing of donor and acceptor semiconducting components is one of the key factors to achieve reasonable device outcome as is the case of **N10**. The reported device performance is among the highest efficiency numbers in the current literature where a number of acceptor units have been conjoined to design a NFA target based on an A–A–A format. This further emphasizes the utility of the design concept used in **N10** and suggests that other acceptor groups at the terminals will be worth examining.

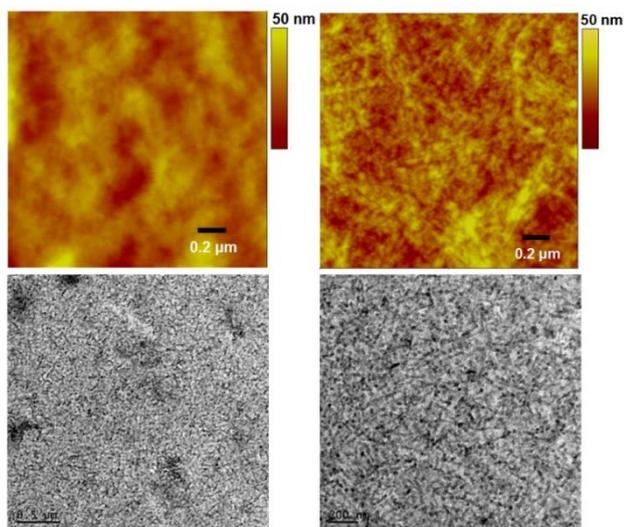


Fig. 4 AFM (upper) and TEM (lower) images for the blend surfaces of P3HT: **N10** showing excellent intermixing of donor and acceptor components. For AFM images, unannealed (left) and annealed (right) surfaces are shown. For TEM images, two scale bars, 500 nm (left) and 200 nm (right), are represented for a better view.

In summary, a NDI core-based NFA, **N10**, with terminal NDI functionalities was designed and synthesized. **N10** possessed a planar format, good solubility, energy levels complementing those of the standard donor polymer P3HT, and excellent thermal stability. Owing to its excellent abilities, such as strong light-harvesting and well-interlaced blend morphology, **N10** was applied in solution-processable BHJ devices as an *n*-type semiconducting component. The P3HT: **N10** blended films provided a very encouraging PCE of 7.65%, a result that not only is among the leading numerals in the current literature but advocates that the studied format is very promising for the futuristic engineering of NFAs.

Conflicts of interest

There are no conflicts to declare.

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