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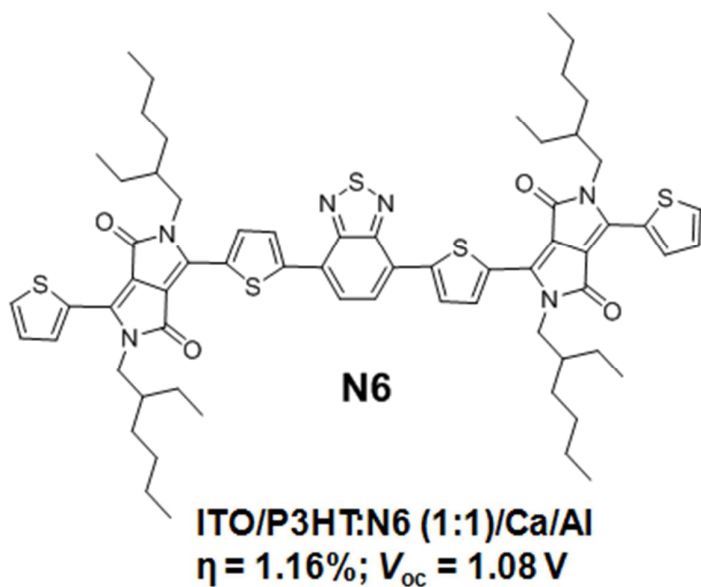
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## Graphical Abstract:



A novel solution-processable electron acceptor based on diketopyrrolopyrrole and benzothiadiazole (**N6**) synthesized, exhibited excellent solubility and thermal stability, and afforded 1.16% power conversion efficiency with high open-circuit voltage (1.08 V).

## COMMUNICATION

## Diketopyrrolopyrrole and benzothiadiazole based small molecule electron acceptor: Design, synthesis, characterization and photovoltaic properties†

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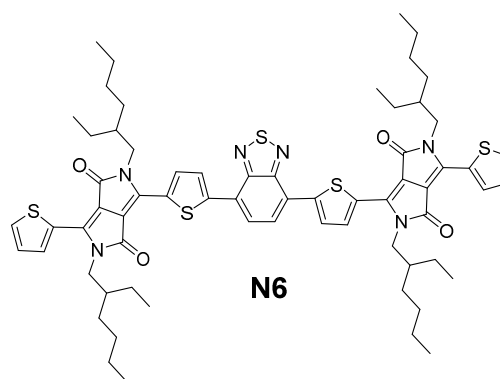
**A novel solution-processable electron acceptor based on diketopyrrolopyrrole and benzothiadiazole building blocks was designed, synthesized, exhibited excellent solubility and thermal stability, and afforded 1.16% power conversion efficiency with high open-circuit voltage (1.08 V) when tested with the classical poly(3-hexylthiophene) electron donor in bulk-heterojunction solar cells. The open-circuit voltage reported here (~1.1 V) is among the highest values for a single bulk-heterojunction device.**

Research into organic-based bulk-heterojunction (BHJ) solar cells has surged in the past decade. These organic cells acquire a huge potential for the fabrication of low-cost, flexible and light weight photovoltaic devices.<sup>1</sup> From the materials perspective, more research has been focused on the design and development of donor materials.<sup>2</sup> Donor functionalities such as archetypal polymer poly(3-hexylthiophene) (P3HT), conjugated polymers and small molecules have been investigated in conjunction with fullerenes and their soluble derivatives, such as [6,6]-phenyl-C<sub>61</sub>-butyric acid methyl ester (PC<sub>61</sub>BM), as electron acceptor materials.<sup>3</sup> Power conversion efficiencies (PCEs) exceed 10% mark for polymers donors and fullerene acceptors.<sup>4</sup> Latter are the choice of dominant electron acceptor materials in BHJ research as they provide high electron mobility, large electron affinity, excellent solubility and ability to form favourable nanoscale network with donor materials.<sup>5</sup> However, these high performing fullerene acceptors are afflicted with a number of potential disadvantages, such as weak absorption in the visible spectrum and restricted electronic tuning via structural modification. Also, a large electron affinity can result in a low open-circuit voltage ( $V_{oc}$ ).<sup>6</sup> These inadequacies with fullerenes provide a strong stimulus to develop non-fullerene electron acceptors which can exert broad absorption, good solubility, high charge carrier mobility and matching energy levels with those of donors.

Recently, non-fullerene electron acceptors have been developed<sup>7</sup> and PCEs exceeding 2% and 4% have been reported using conventional P3HT and non-P3HT donors, respectively.<sup>8</sup> This progress is inspiring, however, there still remain a plethora of

incentives to develop new electron acceptors that will not only overcome the insufficiencies associated with fullerenes but will also exhibit properties such as strong optical absorption, photochemical stability and excellent solubility. One of the common strategies to tailor properties of electron acceptors is to introduce/accumulate electron-withdrawing building blocks and to make an elongated conjugated system. Functionalities such as diketopyrrolopyrrole (DPP), naphthalenediimide (NDI) and perylene diimide (PDI) not only serve this purpose, but also demonstrate good thermal and chemical stability at molecular level. Furthermore, attachment of alkyl chains on the nitrogen atoms of such functionalities not only enhances the solubility, but also helps to generate excellent films without crystallization. Such stated reasons encourage us to pursue research for the development of new electron acceptors based on DPP functionality. The present work is in continuation of our efforts on the development of small molecular chromophores for organic solar cells.<sup>9</sup>

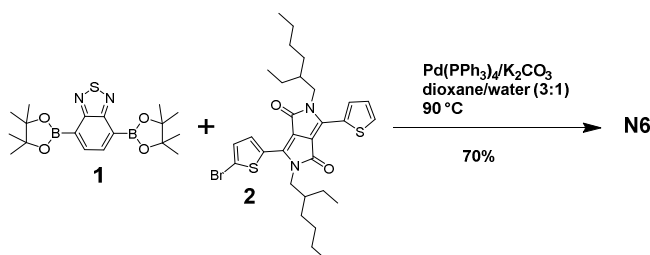
Herein we design, theoretically calculate, synthesize and characterize a DPP-based chromophore (**N6**, Fig. 1) where bulky peripheral DPP substituents are connected through a small-sized benzo[*c*][1,2,5]thiadiazole (BTD) functionality used as a central core.



**Fig. 1** Molecular structure of the investigated non-fullerene electron acceptor **N6**

We envisioned that the connection of DPP and BTD functionalities can provide highly conjugated chromophore with good planarity, high chemical and thermal stability, and with adequate solubility. **N6** was applied in solution-processable BHJ devices as an electron acceptor along with the classical polymer donor P3HT. Solution-processable BHJ devices based on P3HT:**N6** (1:1 w/w) exhibited PCEs as high as 1.16% with high  $V_{oc}$  of 1.08 V; and the  $V_{oc}$  of ~1.1 V is among the highest value reported for solution-processed fullerene-free small molecular organic solar cells.<sup>10</sup> **N6** is the first non-fullerene electron acceptor in the literature with BTD as a core and DPP as arms.

Compound **N6** was successfully synthesized in 70% yield *via* one step Suzuki coupling reaction between commercially available bis-boronic acid pinacol ester derivative of BTD, 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (**1**), and 3-(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)-6-(thien-2-yl)pyrrolo[3,4-*c*]pyrrole-1,4(2*H*,5*H*)-dione (**2**) using tetrakis(triphenylphosphine) palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] as catalyst (See Scheme 1). **N6** was fully characterized by high resolution mass spectrometry (HRMS), <sup>1</sup>H NMR and <sup>13</sup>C NMR spectroscopic techniques. **N6** was found to be highly soluble in a variety of solvents such as chloroform, dichlorobenzene and toluene (for instance, > 20 mg/mL in *o*-dichlorobenzene). High solubility of organic semiconducting chromophores is an essential feature for the fabrication of solution-processable BHJ devices and **N6** fulfils this criterion.

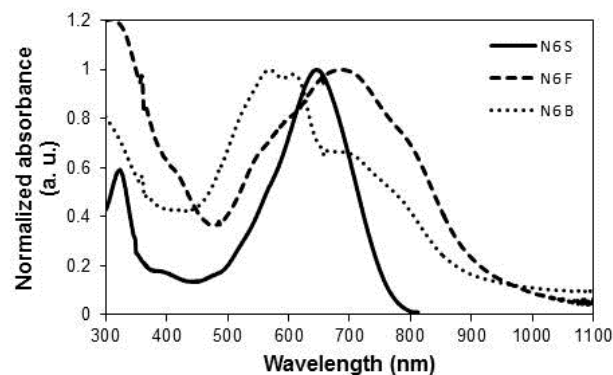


**Scheme 1** Reaction strategy for the synthesis of **N6**

The normalized optical absorption spectra of **N6** in chloroform solution and in thin solid film are shown in Fig. 2. In solution, **N6** exhibits strong absorption with a maximum extinction coefficient of 54,916 M<sup>-1</sup> cm<sup>-1</sup> at 645 nm (8.47 × 10<sup>-6</sup> M). As a thin film, **N6** showed a very broad absorption throughout the visible region (400–1000 nm) and tailing into the near infra-red region (panchromatic absorbance). Thin film absorption is red-shifted by around 40 nm when compared with its solution spectrum. Thin films of blends of P3HT with **N6** (in a ratio of 1:1 w/w) show quenching of the photoluminescence (Fig. S1, ESI<sup>†</sup>), a finding that is consistent with literature reported non-fullerene electron acceptors and indicates that an effective photo-induced charge transfer occurred between **N6** and P3HT in the blend film.<sup>8</sup>

Density functional theory (DFT) calculations using the Gaussian 09 suite of programs<sup>10</sup> and B3LYP/6-311+G(d,p)//B3LYP/6-31G(d) level of theory indicated that orbital densities are evenly distributed over the whole molecular backbone (Fig. S2, ESI<sup>†</sup>), a finding that is consistent with literature reported non-fullerene acceptor materials.<sup>8</sup> The highest occupied molecular orbital (HOMO) energy of **N6** was estimated using Photo Electron Spectroscopy in Air (PESA) (Fig. S3, ESI<sup>†</sup>) and the lowest unoccupied molecular orbital (LUMO) energy was calculated by adding the optical bandgap to the HOMO value. The optical bandgap, estimated from the tangent of the edge of longest wavelength in thin solid film, was 1.35 eV. The estimated HOMO and calculated LUMO energies were found to be -5.06 and -3.71 eV respectively. The difference between the HOMO of donor

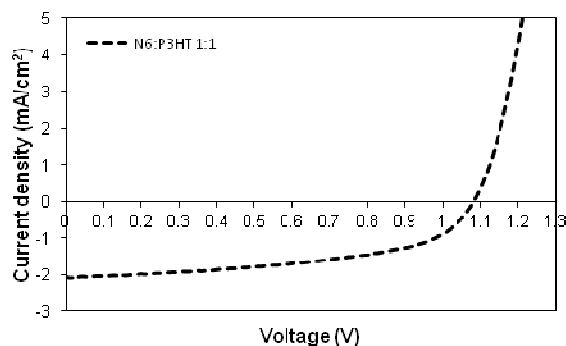
(P3HT; -4.80 eV from PESA) and the LUMO of **N6** (-3.71 eV) was found to be as large as ~1.10 eV, which is promising for achieving a high  $V_{oc}$  in solar cells. **N6** was further tested for its thermal stability so that it can endure rigid device fabricating conditions such as device annealing at a higher temperature. To check the thermal stability, we conducted thermogravimetry (TGA) and differential scanning calorimetry (DSC) analyses. Thermal analyses indicated that **N6** exhibits good thermal stability, a finding that supports temperature annealing of P3HT:**N6** devices at temperatures higher than 100 °C (Fig. S4, ESI<sup>†</sup>).



**Fig. 2.** UV-vis absorption spectra of pristine film (**N6 F**; dashed black curve), 1:1 blend with P3HT (**N6 B**; dotted black curve) and in chloroform solution (**N6 S**; solid black curve).

Once established that **N6** possesses promising optical and electrochemical properties, we tested its efficacy in solution-processable BHJ devices. **N6** was used as a non-fullerene electron acceptor (*n*-type) along with classical donor polymer P3HT (*p*-type). It is well known that BHJ architectures exert higher PCEs by maximising the surface area of interface between the *p*- and *n*-type materials in an active layer. The BHJ device structure used was ITO/PEDOT:PSS (38 nm)/active layer/Ca (20 nm)/Al (100 nm) where the active layer was a solution-processed blend of P3HT and **N6**, a 1:1 blend spin-casted from *o*-dichlorobenzene solution. We<sup>8c</sup> and others<sup>10,11</sup> have shown that thermal annealing of DPP-based small molecule semiconductors can be advantageous for molecular reorganization, high  $V_{oc}$  and superior device efficiency. Consideration of such factors allowed us to anneal our active films at 120 °C for 5 min and the devices were fabricated. BHJ devices showed significant performance and the device parameters,  $V_{oc}$ , short circuit current density ( $J_{sc}$ ), fill factor (FF) and PCE, reached 1.08 V, 2.06 mA/cm<sup>2</sup>, 0.52 and 1.16%, respectively. These fabricated devices yielded very high  $V_{oc}$ , a finding that is consistent with the measured optical band gap between the LUMO of **N6** and the HOMO of P3HT. It is notable that all the devices (a total of ten devices were made) afforded  $V_{oc} > 1$  V and the device parameters reported herein are for the best performing device.  $V_{oc} > 1$  V is not only the highest  $V_{oc}$  among the DPP-based small molecular acceptor semiconductors, but also amongst the highest for single-junction solution-processable BHJ devices. Although the PCEs with the use of non-fullerene electron acceptors have approached 4%,<sup>8</sup> the DPP-based acceptors still lag in design and efficiency. Having said the latter, **N6**-based devices yielded PCE among the top values reported in literature for the DPP-based chromophores, thus providing strong support and incentive for the present research. However, the PCE for the studied devices was low compared to the fullerene-based devices.<sup>12</sup> The lower performance was primarily due to the low short-circuit current and fill factor, which in turn were lower due to charge recombinations and lower electron mobility of the acceptor

materials in the active layer. Representative current-voltage ( $J$ - $V$ ) curve is shown in the Fig. 3.



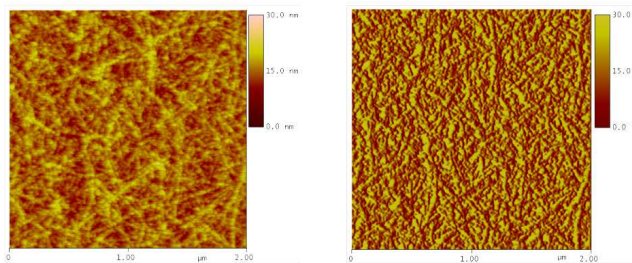
**Fig. 3** Current–voltage curve for the best device based on **N6** and P3HT (1:1 w/w) under simulated sunlight (AM1.5, 1000 W/m<sup>2</sup>). Device structure is: ITO/PEDOT:PSS (38 nm)/Active layer/Ca (20 nm)/Al (100 nm). The active layer was ~52 nm thick.

The analysis of the incident-photon-to-current conversion efficiency (IPCE) measurement of the blend film with a donor/acceptor weight ratio of 1:1 is shown in Fig. S5, ESI†. The blend film of best photovoltaic device showed broad IPCE spectrum from 400 to 1000 nm with an IPCE maximum of ~16% at 560 nm. This suggests that both donor and acceptor components in the BHJ blend made a considerable contribution to the IPCE and  $J_{sc}$ . Even though the IPCE value is moderate, it is an interesting outcome in view of using **N6** with low band-gap conjugated donors such that charge generation could be achieved over a broad range of wavelengths, typically over the whole visible region tailing into the near infra-red region.

To examine the physical microstructure of the blend surface, we used atomic force microscopy (AFM) in tapping mode. The actual surface morphology of the blend film of P3HT:**N6** (1:1 w/w) is shown in Fig. 6. The blend appears to have bush-like morphology with larger crystalline domains and better phase separation with surface roughness of ~3.2 nm. Physically, the blend films were observed as smooth and with no cracks when spin-casted from *o*-dichlorobenzene (3000 rpm/s for 1 min) followed by annealing at 120 °C for 5 min. These processing conditions to generate blend film are in good agreement with the AFM morphology as the use of low-boiling solvents, such as chloroform, resulted in very poor photovoltaic performance. Also, the finding that the BHJ devices comprising **N6** as an acceptor perform better with high-boiling solvent is significant from a processing point of view. Blend film of P3HT:**N6** (1:1 w/w) was analyzed for the measurement of hole and electron mobilities using the transistor technique. Hole and electron mobilities of the order of 10<sup>-5</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> and 10<sup>-6</sup> cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> were observed respectively. Electron mobility, in particular, was low which accounted for lower  $J_{sc}$  and hence moderate PCE. Hole mobility indicated that the presence of **N6** doesn't disrupt the hole-rich P3HT, an observation consistent with the blend film morphology.

Although the material reported in this study achieved a high  $V_{oc}$  with moderate, albeit promising, PCE in solution-processable BHJ devices, there is still an appreciable room to explore device strategies to enhance PCE. The performance can be improved by either using effective interlayer, such as metal oxide interlayer, which can facilitate the efficient charge extraction or by devising processing methods, such as using solvent additives and solvent annealing techniques. Working towards some of these strategies is the subject of on-going work in our laboratories. The discovery of

such materials exhibiting promising optoelectronic properties opens up the way to develop such motifs (based on the central BTD functionality) and paves the way for such materials to be used for other organic electronic applications such as organic field-effective transistors.



**Fig. 4** AFM image for thin film of P3HT:**N6** blend annealed at 120 °C for 5 min (10 mg P3HT, 10 mg **N6** in 1 mL *o*-dichlorobenzene, 3000 rpm/s for 1 min).

In summary, a novel non-fullerene electron acceptor, **N6**, with BTD as a central core and DPP as arms was designed, synthesized and characterized. **N6** possesses excellent solubility, thermal and chemical stability, strong panchromatic absorbance, and appropriate energy levels matching with those of classical donor polymer P3HT. The solution-processable BHJ devices based on P3HT:**N6** blend after annealing at 120 °C for 5 min gave a PCE of 1.16% and a very high  $V_{oc}$  of ~1.10 V, which are among the highest values reported for solution-processable photovoltaic devices using DPP-based non-fullerene acceptors. Our work clearly demonstrates that small molecule acceptors, such as **N6**, with promising optoelectronic properties have an excellent prospect to be at the forefront of non-fullerene acceptor research and enriches the library of acceptors to provide numerous possibilities for donor-acceptor blending recipes to seek high device performance.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Synthetic details & characterization, DFT diagrams, PESA spectrum, TGA, DSC and IPCE spectra of **N6**. See DOI: 10.1039/c000000x/

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