# Solution processable low bandgap diketopyrrolopyrrole (DPP) based derivatives: novel acceptors for organic solar cells<sup>†</sup>

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Novel low bandgap solution processable diketopyrrolopyrrole (DPP) based derivatives functionalized with electron withdrawing end capping groups (trifluoromethylphenyl and trifluorophenyl) were synthesized, and their photophysical, electrochemical and photovoltaic properties were investigated. These compounds showed optical bandgaps ranging from 1.81 to 1.94 eV and intense absorption bands that cover a wide range from 300 to 700 nm, attributed to charge transfer transition between electron rich phenylene-thienylene moieties and the electron withdrawing diketopyrrolopyrrole core. All of the compounds were found to be fluorescent in solution with an emission wavelength ranging from 600 to 800 nm. Cyclic voltammetry indicated reversible oxidation and reduction processes with tuning of HOMO-LUMO energy levels. Bulk heterojunction (BHJ) solar cells using poly(3-hexylthiophene) (P3HT) as the electron donor with these new acceptors were used for fabrication. The best power conversion efficiencies (PCE) using 1: 2 donor-acceptor by weight mixture were 1% under simulated AM 1.5 solar irradiation of  $100 \text{ mW cm}^{-2}$ . These findings suggested that a DPP core functionalized with electron accepting end-capping groups were a promising new class of solution processable low bandgap n-type organic semiconductors for organic solar cell applications.

#### 1. Introduction

Since the last two decades, there have been several synthetic efforts to develop various multifunctional organic semiconductor materials for organic electronic device applications such as organic light emitting diodes, organic field effect transistors (OFETs) and organic photovoltaic cells (OPVs).<sup>1-4</sup> Among all of these devices, flexible organic solar cells hold a lot of promise in terms of a cost effective alternative source for energy using cheap solution based fabrication methods. Bulk heterojunction solar cells (BHJ) based on interpenetrating networks of electron donating polymers and electron accepting derivatives possess the highest efficiencies amongst organic semiconductor based solar cells.5 It is well documented by many groups that OPV devices fabricated using poly(3-hexylthiophene) (P3HT) donor and [6,6]-phenyl-C<sub>61</sub> butyric acid methyl ester (PCBM) acceptor gives power conversion efficiencies (PCE) close to 5%.6 There are several groups worldwide working on developments of new low bandgap donor polymers to enhance PCE further up to 6.0 to 7.6% using PCBM acceptor.<sup>7</sup> Although there are other varieties of new donor materials that have been synthesized for making OPV there are far fewer electron acceptor materials useful for solar cells.8 Reported acceptor materials are primarily perylene and fullerene based materials, which in

synthesis.9 PCBM based devices have relatively high power conversion efficiencies due to its strong tendency to accept electrons from donor semiconducting polymers at short timescales and the formation of suitable nanoscale morphological network with these polymers.<sup>10</sup> Due to poor absorption in the visible spectrum of PCBM and other fullerene derivatives there is need to develop inexpensive alternate electron transporting acceptor materials with high performance. Acceptor materials can be broadly categorized in two classes: polymers or small molecules. Using n-type polymers, efficiencies of up to 1.8% have been attained.11 Polymer acceptors could have some advantages with respect to PCBM due to superior absorption in the visible region and a higher LUMO energy level than PCBM resulting in enhanced open circuit voltages. Polymer acceptors also have some important drawbacks in terms of irregularity in molecular weight from batch to batch, which results in polydispersed materials that affect OPV performance.12 Electron transport is also limited due to various deep traps and defects in acceptor polymer networks, which results in smaller fill factors and lower efficiencies.<sup>13</sup> For all the above reasons, it is desirable to explore more alternative n-type monodispersed small molecule acceptors. Previously our group reported 0.75% efficiency using novel Vinazene based acceptors with P3HT as a donor for OPV devices.<sup>14</sup> By selecting other donor polymers combining with a Vinazene acceptor, efficiency can now reach up to 1.4%.15 A recent report on dicyano-substituted pentacene as an acceptor material with a P3HT donor showed 0.43% efficiency.<sup>16</sup> Low bandgap non-fullerene acceptors can be promising materials to replace PCBM and related acceptor materials. Such materials with strong absorbance, planar structure and good carrier mobility can, in principle, achieve higher efficiencies in OPV

general are relatively difficult to work with in terms of materials

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solar cells. Low bandgap solution processable n-type acceptors can be designed and synthesized using the well-known donor– acceptor (D–A) approach. The addition of various alternating donor/acceptor groups in the conjugated backbone will not only improve the redox properties but also will enhance absorption and intermolecular charge transfer over a wide range of the UV-vis spectrum.

Recently 1.4-diketo-3.6-dithienvlpvrrolo[3.4-clpvrrole (DPP) based materials have attracted tremendous attention in the organic electronics community due to their promising performance in solar cells as well as in field effect transistors.<sup>17</sup> DPP is an interesting block due to the possibility of making various synthetic modifications in terms of attaching solubilising alkyl chains (either straight of branched) on the 3,4-position (i.e. the lactam N-atoms) for getting solution processable materials. Apart from that there is also enormous potential to attach various donor blocks (according to its ionization potential values) at the 2,5-position of the DPP moiety.<sup>18</sup> It has been shown that the solid-state packing,  $\pi$ - $\pi$  intermolecular interactions and optical properties of DPP containing materials are dependent on the nature of these substituents. Additionally, DPP exhibits exceptional photochemical, mechanical and thermal stability, which are prime requirements for making stable organic electronic devices.19

There are several donor DPP based materials (oligomers/ polymers) reported in the literature;16-18 however, none of these are electron accepting/transporting materials. The first design principle for electron-transporting materials is high electron affinity. This can be achieved by the insertion of strong electron withdrawing groups.<sup>20</sup> It has been reported that the introduction of electron-withdrawing groups such as cyano, fluoro, perfluoroalkyl and trifluoromethylphenyl into known conjugated p-type cores gives n-type organic semiconductors.<sup>21-23</sup> Using the same principle, in this work we have designed and synthesized solution processable low bandgap n-type organic semiconductors based on DPP building blocks. DPP is chosen as the core building block for n-type materials development because of its obvious advantages: extremely good stability, very strong light harvesting covering a wide spectrum of the sun light, and strong electron deficiency and facile coupling ability with various aromatic functional groups. The last point is most attractive because chemists can easily tune the LUMOs of the designed materials to desirable levels through coupling with other functional groups. The resulting n-type materials with desirable LUMOs are able to match well with p-type polymers to maximize  $V_{\rm oc}$  of OPV devices. In this paper, a series of DPP oligomers with trifluoromethylphenyl/trifluorophenyl electron withdrawing end-capping groups have been synthesized and characterized. Introduction of the electron withdrawing end capping groups into the molecules aims to further lower the LUMOs of the designed materials which can effectively facilitate charge separation in the donor-acceptor bulk heterojunction OPV devices. Between the DPP core and the electron withdrawing end capping group, one electron donating thienylene group is inserted in order to narrow the bandgap of the molecules thus to expand the absorption spectra of the materials. These materials have been used as acceptors in OPV devices with P3HT as donor and our results show that DPP based oligomers can be used as acceptors achieving efficiencies up to 1% power conversion. This is the

first report of using DPP based acceptor materials for OPV fabrication.

## 2. Results and discussion

### 2.1 Synthesis of conjugated DPP based acceptors

Most of the diketopyrrolopyrrolebased molecules are polymeric materials but there are very few reports of well-defined small molecules,<sup>17</sup> which are easy to purify compared to their polymer counterparts. The strategies used for the synthesis of n-type solution processable small conjugated molecules, described here rely on the concept of strong electron withdrawing functional end capping groups. In particular, these end-groups consist of trifluoromethylphenyl and trifluorophenyl groups attached to the DPP core.

Scheme 1 shows the synthetic procedure to prepare the starting material 2,5-dihydro-1,4-dioxo-3,6-dithienylpyrrolo[3,4-c]pyrrole (2). Compound 2 was prepared with 70% yield by modifying previously reported procedure which involves the reaction of 2-thiophenecarbonitrile (1) with half equivalent of di-n-butyl succinate ester and excess of potassium t-butoxide as strong base using 2-methyl-2-butanol as high boiling point solvent. The reaction was carried out at 110 °C under argon for 24 h and worked up by adding acetic acid, precipitating in water and methanol. In order to make a soluble precursor, compound 2 was reacted with an excess of dodecyl bromide in anhydrous N,Ndimethylformamide (DMF) in the presence of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as base. The reaction was stirred at 120 °C overnight and then worked up by the addition of water and washed with several portions of chloroform. The crude compound N,N'-bis(dodecyl)-3,6-dithienyl-1,4-diketopyrrolo[3,4-c]pyrrole (3) was further purified by column chromatography using chloroform as solvent, resulting in a shiny dark red crystalline solid. This precursor was then dibrominated with N-bromosuccinimide in chloroform and purified by column chromatography, yielding 90% of 3,6-bis-(5-bromo-thiophen-2-yl)-N,N'-bis(dodecyl)-1,4dioxo-pyrrolo[3,4-c]pyrrole (4) material.

Scheme 2 illustrates the synthetic route for all novel n-type organic semiconductors. Compound **TFPVDPP** (tri-fluoromethylphenyl-vinyl end group) isolated from the Suzuki coupling reaction carried out at 80 °C from commercially available *trans*-2-[4-(trifluoromethyl)phenyl]vinyl-boronic acid



**Scheme 1** Synthesis of alkyl-substituted dibromo diketopyrrolopyrrole starting precursor for functionalization.



Scheme 2 Synthesis of diketopyrrolopyrrole (DPP) based novel n-type organic semiconductors. Reagents and conditions: (i) *trans*-2-[4-(tri-fluoromethyl)phenyl]vinyl-boronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 69%; (ii) 4-(trifluoromethyl)phenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 78%; (iii) 3,5-bis(trifluoromethyl)phenylboronic acid, Pd(PPh\_3)\_4, toluene, reflux, 48 h, 50%; (iv) 3,4,5-trifluorophenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 50%; (iv) 3,4,5-trifluorophenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 78%; (iv) 3,4,5-trifluorophenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 50%; (iv) 3,4,5-trifluorophenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 78%; (iv) 3,4,5-trifluorophenylboronic acid, Pd(PPh\_3)\_4, K\_2CO\_3, toluene, reflux, 48 h, 72%.

and 4 (3,6-bis-(5-bromo-thiophen-2-yl)-N,N'-bis(dodecyl)-1,4dioxo-pyrrolo[3,4-c]pyrrole) using Pd(PPh<sub>3</sub>)<sub>4</sub> as a catalyst, and 2M K<sub>2</sub>CO<sub>3</sub> as base in toluene. Boronic acids are nicely soluble in alcohols (compared to boronic esters), for which reason we used a small amount of ethanol in each reaction. Other n-type DPP derivatives such as **TFPDPP** (trifluoromethylphenyl end group), DTFPDPP (ditrifluoromethylphenyl end group), and F3PDPP (trifluorophenyl end group) were synthesized using the abovementioned Suzuki coupling conditions from commercially available 4-(trifluoromethyl) phenylboronic acid. 3,5-bis(trifluoromethyl)phenylboronic acid and 3,4,5-trifluorophenylboronic acid, respectively. The yields are quite good for most of the compounds, ranging from 50 to 78%. All the compounds are dark purple in color and nicely soluble in common organic solvents such as CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, THF and toluene. Materials were purified easily through column chromatography (using chloroform) rather than vacuum sublimation. <sup>1</sup>H and <sup>13</sup>C NMR spectra and MALDI-TOF associated with elemental analysis were employed to confirm the structure and purity of all compounds (see Supporting Information<sup>‡</sup>).

#### 2.2 Optical properties of DPP-acceptors

The absorption spectra of all these n-type DPP derivatives measured in chloroform solutions are shown in Fig. 1a (Table 1). All the materials show absorption bands in the ultraviolet (280–400 nm) and visible/near IR (400–700 nm) regions of the spectrum. A high degree of conjugation between electron donating phenylene-thienylene and the electron accepting DPP core results in a broad and featureless absorption band. The two absorption peaks are attributed to charge transfer associated with phenylene-thienylene moiety (D) and DPP core (A) (Table 1). Compound **TFPVDPP** shows 366 nm absorption peaks in the shorter wavelength region which is red shifted by 30 nm compared to the other derivatives (**TFPDPP**, **DTFPDPP** and **F3PDPP**). This red shift is due to higher conjugation length

induced by vinyl linkage between phenylene and thienylene moiety in the **TFPVDPP** compound. All compounds show absorption maxima in the range of 590–600 nm in the longer wavelength region, except for compound **DTFPDPP**. 20 nm of hypsochromic shift was observed for compound **DTFPDPP** due to stabilization of the LUMO by the two strong electron



Fig. 1 (a) Normalized UV-vis and (b) emission spectrum of TFPVDPP, TFPDPP, DTFPDPP and F3PDPP in chloroform solution.

Compounds	UV-vis $\lambda_{max}/nm^a$	Optical bandgap/ $eV^b$	PL $\lambda_{max}/nm^a$	HOMO <sup>c</sup>	$LUMO^d$	Echem bandgap/eV	$T_{\rm m}/^{\circ}{\rm C}^e$	$T_{\rm d}/^{\circ}{\rm C}^{f}$
TFPVDPP	366, 592	1.81	658	-5.18	-3.55	1.63	229	390
TFPDPP	338, 599	1.94	623	-5.26	-3.52	1.74	231	401
DTFPDPP	339, 569	1.93	610	-5.28	-3.57	1.71	208	398
F3PDPP	331, 595	1.92	619	-5.31	-3.68	1.63	228	330

Table 1 Optical, electrochemical and thermal properties of TFPVDPP, TFPDPP, DTFPDPP and F3PDPP compounds

<sup>*a*</sup> Measured in a chloroform solution. <sup>*b*</sup> Measured from the absorption cut off of the UV-vis spectrum. <sup>*c*</sup> Measured from the oxidation onset of the CV. <sup>*d*</sup> Obtained from the reduction onset of the CV. <sup>*e*</sup> Obtained from DSC measurements. <sup>*f*</sup> Obtained from TGA measurements (temperature at 5% weight loss under nitrogen,  $10 \degree C \min^{-1}$  ramp rate).

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withdrawing trifluoromethyl groups substituted on phenylene moiety. Optical bandgaps calculated from absorption cut off values are in the range of 1.81 to 1.94 eV (Table 1). The lowest bandgap we report is for **TFPVDPP**, which originates from the extension of the  $\pi$ -conjugated system. As per our knowledge these are the lowest bandgap n-type solution processable materials that have been reported. These values are comparable with previously reported oligothiophene containing diketopyrrolopyrrole donor derivatives.<sup>177</sup> Oligothiophenes containing diketopyrrolopyrrole have a higher conjugation length than these n-type materials, although the bandgaps are similar. This is due to enhanced donor–acceptor interactions in n-type materials. Such wide absorbing materials (covering lower as well as higher wavelength regions) are promising for harvesting a larger percentage of the solar spectrum.

The emission spectra for all four materials in chloroform are shown in Fig. 1b (Table 1). Stoke shifts of all compounds vary from 24 to 66 nm, which confirms that these molecules are rigid by nature. These materials exhibit a purple emission colour with the highest maxima recorded at 658 nm for **TFPVDPP**. This particular material shows a red shift of 35 to 48 nm compared to other molecules due to the longest  $\pi$ -conjugation length. **TFPDPP**, **DTFDPP** and **F3PDPP** exhibit emission maxima at 623, 610 and 619 nm, respectively. Compound **DTFDPP** and **F3PDPP** show blue shifts in emission compared to the other two molecules due to strong electron withdrawing groups (two trifluoromethyl and three fluoro) on phenylene. This result clearly indicates that by changing various end-capping electron withdrawing groups we can tune the photophysical properties.

### 2.3 Electrochemical properties of DPP-acceptors

The electrochemical properties of these newly synthesized DPP based acceptors were investigated by cyclic voltammetry in anhydrous dichloromethane. Energy level determination of newly synthesized  $\pi$ -conjugated materials (donor and acceptors) is of crucial importance for use as active components in OPV devices. To achieve high open circuit voltage ( $V_{oc}$ ) and efficient



Fig. 2 Cyclic voltammogram showing the first scan of cathodic and anodic cycles of TFPVDPP, TFPDPP, DTFPDPP and F3PDPP at a scan rate of 100 mV s<sup>-1</sup>. The electrolyte was 0.1 M TBAPF<sub>6</sub>/anhydrous dichloromethane.

charge separation, energy levels of donors and acceptors and their alignment is of high importance in such devices. These energy levels (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)) of newly synthesized materials can be determined by their oxidation and reduction onset potentials. The onset potentials were determined from the intersection of two tangents drawn as the rising current and baseline charging current of the CV traces. The cyclic voltammogram plots of the synthesized DPP based acceptors are shown in Fig. 2. The experiments were carried out under argon at room temperature with a conventional three-electrode arrangement consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3M KCl reference electrode. DPP acceptors TFPDPP, TFPVDPP, DTFDPP show reversible or partially reversible oxidation behavior with two oxidation peaks except F3PDPP, which is attributed to the high electron donating nature of two active blocks (thienvlene and phenylene moieties). HOMO values for all materials were calculated from the corresponding oxidation onsets which were converted to SCE (saturated calomel electrode), based on -4.4 eV SCE energy level relative to vacuum using  $IP = -(E_{ox-onset} + 4.4)$  eV equation. The HOMO values vary from -5.18 to -5.31 eV, indicating that these HOMO values are not only valuable for making stable OPV devices against oxygen oxidation but also useful to transfer holes easily to the PEDOT: PSS (polyethylenedioxythiophene:polystyrene sulfonate) layer due to their close work functions (PEDOT : PSS has a work function of 5.2 eV). TFPVDPP shows the highest HOMO value (-5.18 eV) compared to other derivatives, which is due to a reduction of oxidation onset in extended conjugated molecules. A vinyl group with phenylene enhances the conjugation of TFPVDPP.

These newly synthesized acceptors also exhibit partially or fully reversible reduction cycles due to central electron withdrawing DPP core and end capping groups. LUMO values were also calculated (similar way like HOMO value determination) from the corresponding reduction onsets using  $EA = -(E_{red-onset})$ + 4.4) eV. LUMO values calculated in the range of -3.52 to -3.68 eV, which is about 0.5 eV closer to vacuum than that of the well-known acceptor PCBM C60 energy level (-4.10 eV). Lowest LUMO values were found for compounds DTFPDPP and F3DPP due to a higher number of electron withdrawing groups (two trifluoromethyl and three trifluoro) on the phenyl end capping ring. Examining Table 1, we can compare the effect of the various end-capping groups on the energy levels and bandgaps. Electrochemical bandgaps obtained from HOMO-LUMO differences were found to be in good agreement with the optical bandgaps calculated from the UV-vis absorption onset.

### 2.4 Thermal properties of DPP-acceptors

The thermal properties of all the synthesized DPP based acceptor materials were determined by repetitive heating–cooling cycles using differential scanning calorimetry (DSC) analyses at a heating rate of 10 °C min<sup>-1</sup>. All the DPP derivatives show crystalline to isotropic transitions with a melting temperature  $(T_m)$  varying from 208 to 229 °C in DSC thermogram (Table 1 and also see Supporting information<sup>‡</sup>). For compounds **TFPVDPP**, **TFPDPP** and **F3PDPP**, the melting temperatures are quite similar (228 to 231 °C) due to the similarity of aromatic conjugated blocks. The highest melting temperature (231 °C) was recorded for compound **TFPDPP** due to its more rigid nature. The lowest melting temperature of 208 °C was recorded for compound **DTFPDPP** due to two trifluoromethyl groups on each of the end capping phenylene ring. Thermal decomposition of all the DPP acceptor materials was carried out using thermogravimetric analysis (TGA). Thermal decomposition temperatures ( $T_d$ , 5% wt loss) for **TFPVDPP**, **TFPDPP**, **DTFPDPP** and **F3DPP** were observed at 390, 401, 398 and 330 °C respectively (Table 1 and Fig. S8‡). This observation clearly indicates good thermal stability of these materials even at high temperatures, required for vacuum deposition.

### 2.5 DFT electronic structure calculation

Density functional theory (DFT) calculations on their electronic state were performed using DMol<sup>3</sup> module (at the level of GGA-PW91<sup>24</sup>/DNP in the Materials Studio Modelling software package (Accelrys Inc.) to understand the properties of these derivatives (HOMO–LUMO trend and planarity of the material arises from donor–acceptor interactions). The optimized geometry, electron density distribution of HOMO and LUMO of newly synthesized DPP based materials are shown in Fig. 3. All



Fig. 3 The optimized geometries and electron density isocontours of HOMO and LUMO of TFPVDPP, TFPDPP, DTFPDPP and F3PDPP obtained at the BLYP/DMol<sup>3</sup>-PW92 level.

Compounds	НОМО	LUMO	Molecular length of aromatic part/Å	Dihedral angles $(\theta / \circ)$	Calculated distance between carbonyl oxygen and thiophene hydrogen of DPP/Å
TEDUDDD	4.9.6	2.06	22.01	5 22/2 70	2.00
TEPVDPP	-4.86	-3.86	23.91	5.33/2.70	2.06
TFPDPP	-4.94	-3.76	19.51	18.98/19.10	2.11
DTFPDPP	-5.13	-3.97	19.54	17.96/18.03	2.10
F3PDPP	-4.97	-3.76	19.29	22.46/24.03	2.14

 Table 2
 Summary of DFT derived HOMO–LUMO energies, aromatic molecular length, dihedral angles between phenyl and DPP, and the distances calculated between carbonyl oxygen and thiophene hydrogen for TFPVDPP, TFPDPP, DTFPDPP and F3PDPP materials

the isocontour values are  $\pm 0.02$ . Theoretical calculated HOMO-LUMO gaps, aromatic conjugated lengths of the molecule and distances between hydrogen (positioned on thiophene) and oxygen (positioned on carbonyl group) of the DPP n-type derivatives are presented in Table 2 (also see Supporting Information<sup>‡</sup>). In all materials, the HOMOs and LUMOs are localized along the conjugated backbone. Such localization of the HOMO/LUMO orbital on D-A units has been commonly observed in previous theoretical studies of D-A materials.25 The calculated HOMO/LUMO eigenvalues of this energy optimized structures are listed in Table 2. The present DFT computed predicted HOMO/LUMO values show similar trends which we observed for electrochemical and optical analysis. The theoretically predicted HOMO and LUMO energy levels are about 0.3 to 0.4 eV higher than experimentally calculated values. This is related with various effects such as conformational order in bulk state, effect of solvent and electrolyte which are not taken into account. Two trifluoromethyl substituted phenyl based material DTFPDPP shows the lowest LUMO values due to two electron withdrawing groups; which follows a similar trend observed

experimentally (-3.97/-3.57 eV). The highest HOMO value (determined both theoretically and experimentally) are for **TFPVDPP** (-5.18/-4.86 eV) which is due to extended conjugated molecular length which is around 23.91 Å. Other materials **TFPDPP**, **DTFPDPP**, and **F3DPP** show conjugation lengths of 19.51, 19.54 to 19.29 Å, respectively. The conjugated aromatic part of the molecule plays a crucial role for the charge delocalization, which is very important for charge transport. As the conjugation length increases, the bandgap reduces (**TFPVDPP** shows the highest aromatic conjugation length as well as the lowest bandgap).

For charge delocalization, planarity of the material is important. Planarity of all these newly synthesized materials was predicted from the dihedral angles between end capping groups and the DPP core. The lowest dihedral angles were reported for **TFPVDPP** which were 5.33/2.70 degrees, respectively, which is the most planar molecule; whereas for other materials we studied, these values vary from 17 to 24 degrees. It is already reported that the DPP moiety has a strong tendency of  $\pi$ - $\pi$ stacking and hydrogen bonding interactions<sup>17,18</sup> which helps



Fig. 4 Normalized UV-vis spectrum of TFPVDPP, TFPDPP, DTFPDPP and F3PDPP blended with P3HT active thin film layer deposited on glass from toluene and chloroform solution.

charge carrier transport.<sup>17</sup> The theoretically calculated distance between carbonyl oxygen and thiophene hydrogen (responsible for intra and intermolecular H-bonding interactions) in the DPP core is around 2.1 Å. DFT computed studies of these molecules are very helpful for predicting the various properties such as conjugation length, planarity, and electron density distribution before synthesis.

# 2.6 UV-vis absorption spectroscopic measurement of P3HT donor and DPP acceptor blends

Absorption characteristics of spin coated films prepared from the blends of P3HT donor and these newly synthesized DPP based acceptors (1:2 blend ratios) processed from two different solvents toluene and chloroform are shown in Fig. 4. It can be seen that mixtures of the two materials absorb strongly throughout the range of 300 nm to 750 nm. The absorption of the blends is relatively high in the 450 to 700 nm range, and indicates the higher optical density and wide absorbance of DPP n-type materials compared to PCBM. It is quite instructive to note that P3HT donor with new acceptors TFPVDPP and TFPDPP blended films processed from toluene shows higher red shift of 25–30 nm than the chloroform processed thin films. Whereas DTFDPP and F3PDPP blended with P3HT films processed from chloroform shows a slight red shift of 10-20 nm compared with toluene processed thin films. This observation suggests that toluene is a better solvent for TFPVDPP and TFPDPP whereas chloroform is a good solvent for DTFDPP and F3PDPP. Such a kind of red shift in thin films processed from various solvents may be due to evaporation ability of the solvent and solventsolute interaction for getting strong  $\pi$ - $\pi$  stacking during spin coating. Red shift in solid state not only improves the harvesting of more sunlight but also helps for getting better charge dissociation at the interface of D-A nanostructures. From this explanation we can predict that devices fabricated from toluene (using TFPVDPP and TFPDPP blended with P3HT) and chloroform (F3PDPP blended with P3HT) can show promising OPV solar performance. Indeed at least for three n-type materials (out of four) processed from appropriate solvents using P3HT donor we got a performance in the range of 0.5 to 1.0%. More details about these devices are explained in the photovoltaic properties part.

# 2.7 Photovoltaic properties using new acceptor and P3HT donor BHJ devices

Bulk heterojunction solar cell devices were fabricated with a transparent indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) : poly(styrene sulfonate) (PEDOT : PSS) front electrode. The active layers were spin coated from toluene and chloroform solvents using the blends of the P3HT donor and newly synthesized acceptor in a blend ratio of 1 : 2, respectively. This combination was found to be the most optimum after trying various blend ratios. The thin films processed from two different solvents were used to see the effect on device performance with respect to solvent-blend feasibility. On top of the active layer, a thin 10 nm layer of Ca was evaporated followed by the evaporation of a silver electrode as a cathode and reflecting back electrode. The surface of the active area was 9 mm<sup>2</sup> with the



Fig. 5 (a) Energy level diagram for the OPV device structure using a P3HT donor and newly synthesized **TFPVDPP**, and **TFPDPP** acceptors. (b) The device structure and (c) I-V curves of the optimized devices with the configuration of ITO/PEDOT : PSS/P3HT : new acceptor/ Ca(10 nm)/Ag(100 nm) using P3HT as the donor and **TFPVDPP**, **TFPDPP**, **DTFPDPP** and **F3PDPP** as the acceptor blended thin film under AM 1.5G 100 mW cm<sup>-2</sup>.

average thickness of an active layer within the same range  $(100 \pm 20 \text{ nm})$ . The devices with a structure of ITO/ PEDOT : PSS/P3HT : DPP acceptors (1 : 2 wt %)/Ca/Ag were characterized in an inert gas glove box under the illumination of simulated AM 1.5G solar irradiation with a calibrated power intensity of 100 mW cm<sup>-2</sup>. Current-voltage (I-V) characteristics of the devices using newly synthesized acceptors with a P3HT donor were measured and are presented in Fig. 5. The photovoltaic parameters such as short circuit current density  $(J_{sc})$ , open circuit voltage (Voc), fill factors (FF) and power conversion efficiencies (PCE) for all devices are reported in Table 3. It can be seen that the best power conversion efficiency of 1.00% has been achieved for devices using a TFPDPP acceptor with  $V_{\rm oc} = 0.81$  V,  $J_{\rm sc} = 2.36$  mA cm<sup>-2</sup>, and a fill factor FF = 52% processed from toluene. As per our knowledge, to date this is the highest PCE value achieved using n-type DPP based low bandgap solution processable material for OPV devices. Another promising acceptor from the series is TFPVDPP which gives a performance around 0.58% PCE with  $V_{\rm oc} = 0.64$  V,  $J_{\rm sc} = 1.70$  mA cm<sup>-2</sup>, and a fill factor FF = 53%. For the **TFPVDPP** we got a lower  $V_{oc}$  than **TFPDPP**, this is due to the lower LUMO of this material.

**Table 3** Photovoltaic properties of P3HT and **TFPVDPP**, **TFPDPP**, **DTFPDPP** and **F3PDPP** acceptor based devices (spin coated from toluene and chloroform solutions). Measurement under AM 1.5 at 100 mW cm<sup>-2</sup>.  $J_{sc}$ : short circuit current density,  $V_{oc}$ : open circuit voltage, and PCE: power conversion efficiency

Donor	Acceptor	Solvent	V <sub>oc</sub> /V	$J_{\rm sc}/{ m mA~cm^{-2}}$	FF (%)	PCE (%)
РЗНТ	TFPVDPP	Toluene	0.64	1.70	53	0.58
P3HT	TFPDPP	Toluene	0.81	2.36	52	1.00
P3HT	DTFPDPP	Toluene	0.28	0.05	36	0.05
P3HT	<b>F3PDPP</b>	Toluene	0.53	1.88	29	0.28
P3HT	TFPVDPP	Chloroform	0.79	1.06	32	0.27
P3HT	TFPDPP	Chloroform	0.90	1.04	27	0.25
P3HT	DTFPDPP	Chloroform	0.71	0.85	23	0.14
РЗНТ	F3PDPP	Chloroform	0.65	2.70	32	0.56

In the experiment, we also studied the effect of various solvents used for the spin coating of the blends on the device performance. Using the same acceptors (TFPVDPP and TFPDPP) processed from chloroform,  $J_{sc}$  decreased from 1.70 to 1.06 mA cm<sup>-2</sup> and 2.36 to 1.04 mA cm<sup>-2</sup>, respectively. The  $V_{oc}$  (0.81 V) value reported for the best device is higher than the  $V_{\rm oc}$  value (0.60 V) of a typical P3HT : PCBM solar cell. F3PDDP processed from chloroform solvent showed the highest performance of 0.56% PCE with  $V_{\rm oc} = 0.65$  V,  $J_{\rm sc} = 2.70$  mA cm<sup>-2</sup>, and a fill factor FF = 32%. Photovoltaic properties of these acceptors are very sensitive to molecular structure and solvents; currently we are studying the structure-solvent relationship in terms of PCE. The effect of using various solvents for processing on OPV performance was earlier reported by Janssen et al. using DPP based donor materials.<sup>17d</sup> In case of Vinazene acceptors, by varying side chain (hexyl vs. ethyl hexyl) tunes the solubility of material and affects on the OPV performance.<sup>14</sup> Molecular organization in solid state through solution processing and appropriate film nanomorphology are very important for efficient charge separation and collection. Further enhancement in optical density in the range of 300 to 450 nm and extended conjugation up to 900 nm can improve PCE further with selecting proper side chain and end capping groups. Based on the above experimental results, these new DPP-containing n-type low bandgap materials are promising candidates for organic photovoltaic devices. Most of the materials show performance in the range of 0.5 to 1%, indicating that these novel acceptors can be optimized further. This includes optimization in solar cell structures, processing conditions, active layer morphology, usage of various donor polymers and designing of new n-type DPP materials to significantly improve the solar cell performance.

# 3. Conclusions

Novel solution processable low bandgap DPP based organic semiconductor acceptors with trifluoromethylphenyl and trifluorophenyl end capping electron withdrawing groups have been designed, synthesized and characterized. The optical absorption and electrochemical potentials were used to determine the relevant HOMO and LUMO energy levels. Optical bandgaps of all these acceptors were calculated in the range of 1.64 to 1.82 eV. Solution processed thin film photovoltaic devices of the corresponding novel acceptors with P3HT donor exhibited promising performance. Photovoltaic performances of these new acceptor materials are quite sensitive with molecular structure and processing conditions. Higher PCE were recorded for **TFPDPP** and **TFPVDPP** acceptors with trifluoromethylphenyl end capping groups. The best power conversion efficiency of 1.00% has been achieved for devices using **TFPDPP** acceptors with  $V_{\rm oc} = 0.81$  V,  $J_{\rm sc} = 2.36$  mA cm<sup>-2</sup>, and a fill factor FF = 52% processed from toluene under simulated AM 1.5G solar irradiation of 100 mW cm<sup>-2</sup>. These findings suggest that DPP moiety can be used as a promising building block to synthesize low bandgap solution processable acceptors for organic solar cell applications with further optimization. More work on such DPP functionalized n-type material is going on in our laboratory and will be reported in due course.

# 4. Experimental

### 4.1 Material and characterization

All the chemicals were purchased from Sigma-Aldrich, Strem and used without further purification. All reactions were carried out using Schlenk techniques in an argon or nitrogen atmosphere with anhydrous solvents. <sup>1</sup>H and <sup>13</sup>C NMR data were performed on a Bruker DPX 400 MHz spectrometer with chemical shifts referenced to residual CHCl<sub>3</sub> and H<sub>2</sub>O in CDCl<sub>3</sub>. Matrix assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a Bruker Autoflex TOF/TOF instrument using dithranol as a matrix. UV-Vis spectra were recorded on a Shimadzu model 2501-PC. Photoluminescence (PL) spectra were measured on a Perkin-Elmer (LS50B) spectrofluorimeter. Cyclic voltammetry experiments were performed using an Autolab potentiostat (model PGSTAT30) by Echochimie. All CV measurements were recorded in dichloromethane with 0.1 M tetrabutylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV s<sup>-1</sup>). The experiments were performed at room temperature with a conventional three-electrode configuration consisting of a platinum wire working electrode, a gold counter electrode, and an Ag/AgCl in 3 M KCl reference electrode. Differential scanning calorimetry (DSC) was carried out under nitrogen on a TA Instrument DSC Q100 instrument (scanning rate of 10 °C min<sup>-1</sup>). Thermal gravimetric analysis (TGA) was carried out using a TA Instrument TGA Q500 instrument (heating rate of 10 °C min<sup>-1</sup>). X-Ray diffraction patterns of thin films deposited at room temperature on the Si/SiO2 substrate were obtained with a PANalytical X'PERT PRO system using Cu-Ka source in air. SEM images were obtained with a JEOL FESEM JSM-6700F molecular imaging digital instruments microscope in air.

### 4.2 Device fabrication and characterization

The fabrication of a bulk heterojunction organic solar cell (BHJ-OSC) involved several consecutive steps. For material preparation, poly(3-hexylthiophene) (P3HT) purchased from Rieke was used as a donor. Four new n-type materials namely TFPVDPP, TFPDPP, DTFPDPP and F3PDPP were used as acceptors. 10 mg mL<sup>-1</sup> for P3HT and 20 mg mL<sup>-1</sup> for DPP n-type materials concentrations were used for making blends. Blends (weight ratio = 1:2) were prepared separately using chloroform and toluene, two different solvents, respectively. The solutions were stirred until desired homogeneity was achieved then they were mixed with the same solvent system and stirred overnight. For device fabrication, 160 nm thick indium tin oxide (ITO)-coated glass, with an average sheet resistance of  $14\Omega/\Box$ , was used as the substrate for BHJ-OSC. The ITO was patterned using a standard photolithography process. The ITO/glass substrates were cleaned in detergent (30 min), distilled water (20 min), acetone (15 min) and isopropanol (20 min). The substrates were then baked at 80 °C in an oven to remove residual solvents. The dried substrates were subjected to oxygen plasma cleaning for 10 min prior to the spin coating of a 40 nm thick PEDOT: PSS hole transporting layer (Baytron P). Subsequently, P3HT : n-type material blends were spin coated on top of a PEDOT : PSS layer with a spinning speed of 1500 rpm for 60 s in an inert gas glove box. For the cathode, calcium and silver with thicknesses of 10 nm and 100 nm, respectively were evaporated through a shadow mask at a pressure of 8  $\times$  10<sup>-5</sup> Pa to obtain devices with an active area of 9 mm<sup>2</sup>. The performances of the BJH-OSC were characterized in an inert gas glove box under illumination of simulated AM1.5G solar irradiation with a calibrated power intensity of  $100 \text{ mW cm}^{-2}$ .

### 4.3 Synthetic procedures

The starting precursor compound 2,5-dihydro-1,4-dioxo-3,6dithienylpyrrolo[3,4-c]-pyrrole (DPP) was synthesized in good yield following a previously reported procedure which contains the reaction of 2-thiophenecarbonitirile with 0.5 eq. of di-n-butyl succinate ester and an excess of potassium t-butoxide using 2-methyl-2-butanol as solvent. To prepare soluble derivative 3,6-bis-[2,2']bithiophenyl-5-yl-2,5-di-n-dodecylpyrrolo[3,4-c]pyrrole-1,4-dione (DD-DPP), we further did alkylation of DPP using 3 eq of *n*-dodecylbromide with 3 eq of anhydrous  $K_2CO_3$  in the presence of anhydrous DMF solvent. Dibromo derivatives of alkylated DPP (DB-DD-DPP) was synthesized by additional bromination with N-bromosuccinimide in anhydrous chloroform and the crude compound was purified by column chromatography using chloroform as eluent and the overall yield was recorded around 40%. This core compound was used for further functionalization using suitable end groups for making novel n-type solution processable low bandgap materials.

**4.3.1.** Synthesis of TFPVDPP. Dibromo-DD-DPP compound (0.300 g, 0.37 mmol), *trans*-2-[4-(trifluoromethyl)phenyl]vinyl-boronic acid (0.204 g, 0.944 mmol, 2.5 eq.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30mg, 0.025 mmol) were added to a 50 mL schlenk flask and subjected to three vacuum/argon refill cycles. Argon degassed toluene

(15 mL); aqueous 2M K<sub>2</sub>CO<sub>3</sub> (7 mL) and ethanol (3 mL) were added to the above mixture and stirred for 20 min under argon. After addition of solvent three more time vacuum/argon cycles were repeated to make sure about the oxygen exclusion. The reaction mixture was heated at 80 °C for 24 h and monitored *via* TLC. After completion of the reaction, toluene was removed using a rotovap and the product extracted with chloroform, then successively washed with water, and dried over MgSO<sub>4</sub>. Removal of the solvent afforded the crude product which was then purified using column chromatography (silica gel, chloroform as eluent) and gave the product as a dark purple crystalline solid (0.250 g, 69%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, 6 H), 1.15–1.47 (m, 36 H), 1.78 (t, 4 H), 4.11 (t, 4 H), 7.10–7.15 (d, 2H), 7.28–7.38 (dd, 4 H), 7.62 (dd, 8 H), 8.92(d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 161.26, 147.27, 139.74, 139.14, 136.14, 130.16, 129.84, 129.36, 129.06, 128.29, 126.73, 125.81, 125.77, 125.74, 125.41, 123.16, 122.70, 108.83, 42.32, 31.88, 29.99, 29.64, 29.62, 29.60, 29.53, 29.31, 29.24, 26.90, 22.63, 14.02.

Calculated for C<sub>56</sub>H<sub>66</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 68.83, H 6.81, F, 11.66, N 2.87, O 3.27, S 6.93%; Found: C 68.78, H 6.76, N 2.77, S 6.96%.

**4.3.2.** Synthesis of TFPDPP. This reaction was carried out using the same way which we mentioned above using the dibromo-DD-DPP compound (0.300 g, 0.37 mmol), 4-(tri-fluoromethyl) phenylboronic acid (0.180 g, 0.94 mmol, 2.5 eq.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30 mg, 0.025 mmol) in toluene (15 mL); aqueous 2M K<sub>2</sub>CO<sub>3</sub> (7 mL) and ethanol (3 mL) solvent mixture under argon. After three vacuum/argon cycles the mixture was heated at 80 °C for 24 h then monitored *via* TLC. Removal of the solvent afforded the crude product which was then purified using column chromatography (silica gel, chloroform as eluent) and gave the product as dark purple solid (0.270 g, 78%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.88 (t, 6 H), 1.15–1.47 (m, 36 H), 1.80 (t, 4 H), 4.09 (t, 4 H), 7.52 (d, 2 H), 7.65 (d, 4 H), 7.78 (d, 4 H), 8.93(d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 161.23, 147.54, 139.39, 136.48, 136.43, 136.42, 131.02, 130.70, 130.37, 130.05, 127.96, 126.26, 126.20, 126.16, 126.12, 126.09, 125.99, 125.83, 125.25, 122.55, 119.84, 108.56, 42.34, 31.87, 29.99, 29.62, 29.61, 29.57, 29.51, 29.31, 29.22, 26.88, 22.63, 14.02.

Calculated for  $C_{52}H_{62}F_6N_2O_2S_2$ : C 67.51, H 6.75, F 12.32, N 3.03, O 3.46 S 6.93%; Found: C 67.48, H 6.74, N 2.92, S 6.62%. MS (MALDI-TOF) m/z 924.57 (M). calcd. for

 $C_{52}H_{62}F_6N_2O_2S_2 = 924.42.$ 

**4.3.3.** Synthesis of DTFPDPP. This reaction was carried out using the same way which we mentioned above using dibromo-DD-DPP compound (0.300 g, 0.37 mmol), 3,5-bis (trifluoromethyl) phenylboronic acid (0.243 g, 0.945 mmol, 2.5 eq.) and Pd(PPh\_3)<sub>4</sub> (30 mg, 0.025 mmol) in toluene (15 mL); aqueous 2M K<sub>2</sub>CO<sub>3</sub> (7 mL) and ethanol (3 mL) solvent mixture. After three vacuum/argon cycles the mixture was heated at 80 °C for 24 h then the reaction mixture was worked up using an extraction method. Removal of the solvent afforded the crude product which was then purified using column chromatography (silica gel, chloroform as eluent) and gave the product as a dark purple solid (0.200 g, 50%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 0.87 (t, 6 H), 1.15–1.47 (m, 36 H), 1.79 (t, 4 H), 4.10 (t, 4 H), 7.28–7.31 (s, 1H), 7.52–7.70 (dd, 2 H), 7.86 (s, 1H), 8.05 (d, 2 H), 8.80–9.00 (dd, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 161.25, 144.93, 140.88, 138.49, 136.04, 135.77, 135.74, 135.57, 135.35, 135.28, 135.24, 132.92, 132.59, 131.69, 131.15, 131.01, 130.79, 129.67, 128.70, 128.01, 126.55, 126.49, 125.87, 124.37, 121.80, 121.66, 108.98, 108.05, 107.83, 42.33, 31.88, 29.93, 29.66, 29.59, 29.57, 29.54, 29.52, 29.21, 26.81, 22.64, 14.04. Calculated for  $C_{54}H_{60}F_{12}N_2O_2S_2$ : C 61.12, H 5.70, F 21.48, N

2.64, O 3.02, S 6.04%; Found: C 61.08, H 5.68, N 2.57, S 6.10%. MS (MALDI-TOF) m/z 1060.73 (M). calcd. for  $C_{54}H_{60}F_{12}N_2O_2S_2 = 1060.39$ .

**4.3.4.** Synthesis of F3PDPP. Dibromo-DD-DPP compound (0.300 g, 0.37 mmol), 3,4,5-trifluorophenylboronic acid (0.243 g, 0.945 mmol, 2.5 eq.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (30mg, 0.025 mmol) were added to a 50 mL Schlenk flask and subjected to three vacuum/ argon refill cycles. Argon degassed toluene (15 mL), aqueous 2M  $K_2CO_3$  (7 mL) and ethanol (3 mL) were added to the above mixture and stirred for 20 min under argon. After three vacuum/ argon cycles the mixture was heated at 80 °C for 24 h then monitored *via* TLC. After completion of the reaction, solvent was removed on rotovap and the product extracted with chloroform, then successively washed with water, and dried over MgSO<sub>4</sub>. Removal of the solvent afforded the crude product which was then purified using column chromatography (silica gel, chloroform as eluent) and gave the product as a dark purple crystalline solid (0.240 g, 72%).

<sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.87 (t, 6 H), 1.10–1.47 (m, 36 H), 1.78 (t, 4 H), 4.10 (t, 4 H), 7.25 (d, 4 H), 7.40 (d, 2 H), 8.87 (d, 2 H). <sup>13</sup>C NMR (CDCl<sub>3</sub>): 161.27, 139.30, 136.31, 130.04, 125.80, 110.48, 110.32, 110.25, 108.66, 87.53, 73.04, 66.83, 42.31, 37.01, 31.87, 29.98, 29.60, 29.58, 29.55, 29.49, 29.30, 29.22, 26.86, 22.63, 14.03. Calculated for C<sub>50</sub>H<sub>58</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub>: C 66.94, H 6.52, F 12.71, N 3.12, O 3.57, S 7.15%; Found: C 66.88, H 6.46, N 3.02, S 7.02%. MS (MALDI-TOF) *m/z* 896.24 (M). calcd. for C<sub>50</sub>H<sub>58</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>S<sub>2</sub> = 896.38.

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