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# Effect of fluorine on optoelectronic properties in D<sub>I</sub>-A-D<sub>II</sub>-A-D<sub>I</sub> type organic molecules: A combined experimental and DFT study

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# A R T I C L E I N F O

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# ABSTRACT

The impact of the substitution of fluorine atom/atoms on the optoelectronic features of organic molecules having  $D_{I}$ -A- $D_{II}$ -A- $D_{I}$  type architecture is examined in the current work. The three synthesized organic molecules (**SMD1**, **SMD2** and **SMD3**) comprise of a dithienopyrrole (DTP) derivative as a central donor ( $D_{II}$ ), which is flanked between two benzothiadiazole (BT) moieties (electron acceptors, A). The BT core on each of two ends is joined to an electron-donating benzodithiophene (BDT) derivative ( $D_{I}$ ). The **SMD1**, **SMD2** and **SMD3** are substituted with 0, 2 and 4 fluorine atoms on their BT moiety respectively. The assistance of DFT methods is taken to evaluate the influence of fluorine on reorganization energies, ionizing potential and electron affinity of molecules. The thermal stability of molecules is mapped by TGA studies. Cyclic voltammetry studies are carried out to comprehend the characteristics of highest molecular orbital, lowest unoccupied molecular orbital and the bandgap of molecules, which are also supported by DFT methods. The molecules displayed better absorption properties in the near-infrared (NIR) region, excellent solution processability in a variety of organic solvents, low bandgap and optimum thermal toughness to make them applicable in the construction of OBHJSCs to play the role of donor materials when connected with acceptors like fullerene derivatives.

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#### 1. Introduction

Recently, the enhancement of power conversion efficiency (PCE) of organic bulk heterojunction solar cells (OBHJSCs) has been the center of focus in the field of organic photovoltaics (OPV) and has gathered a number of scientific reports, which elucidate the significance of meticulous molecular design, morphology organization and appropriate molecular orientation in achieving better PCEs for OBHJCs [1–4]. Generally, increased amounts of short-circuit current density ( $J_{SC}$ ) and open-circuit voltage ( $V_{OC}$ ) contribute to the elevation of PCE of OBHJSCs along with a contribution from the elevated magnitude of fill factor (FF) of the devices. In this regard, organic molecules having interconnected donor (D) and acceptor (A) moieties offer to produce better OBHJSCs since they can fulfill the conditions to have good PCE [5,6].

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In particular, designing of organic molecules with substitution of the electron-donating groups on D and inclusion of electronattracting groups on A plays a critical role in tuning optoelectronics (and hence altering PCE) of a material. In the recent past, there have been numerous research articles, which illustrate the impact of substituting A with electron-withdrawing groups (majorly fluorine atom) [7-20] on the optoelectronic properties of a material having various types of donor-acceptor materials. Fluorination of acceptor core is an effective approach to obtain the materials with good PCE since, i) it fine-tunes the energetics of frontier molecular orbitals (by lowering energies of highest occupied molecular orbital) without compromising bandgap [21], ii) improves molecular ordering by dipole moment induced along carbon-fluorine bond [21], iii) imposes no steric hindrance due to its smaller size and hence helps in planarizing the molecules [14], iv) triggers non-covalent interactions through F...S and C-F...H bonds [12,22], v) strong electron-attracting nature of F causes material to be hydrophobic, which provides stability to material in environmental conditions [23-28], vi) provide high fill factor, open-circuit voltage and short circuit current





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density, which are requisite conditions for a good OPV device [8-13,15-17,19,20,29-36].

Though incorporation of fluorine bestows a material with several benefits; it poses some drawbacks like reduced solubility in organic solvents, energy levels that are not suitable for charge transport and higher aggregation of polymers in active layers of polymer solar cells [21,37,38]. Hence, the extent of fluorination or the number of fluorine atoms substituted needs to be optimized in order to get the optimal performance of an OPV, which widens the scope of research in this regard.

Keeping all the above facts in mind, our present work is designed to synthesize three D<sub>I</sub>-A-D<sub>I</sub> type molecules, each having a varying number of fluorine atoms in the molecular backbone. In this work, the synthesis of three organic molecules designated as **SMD1**, **SMD2** and **SMD3** (Fig. 1) having zero, two and four fluorine atoms respectively at selective places is reported. The molecule 4,8-bis{(2-ethylhexyl)oxy}-4,8-dihydrobenzo{1,2-b:4,5b'}dithiophene (OBDT) is employed as a terminal donor (D<sub>1</sub>) at two ends and 4-{2-ethylhexyl}-4H-dithieno{3,2-b:2',3'-d}pyrrole (DTP) is used as a central donor (D<sub>II</sub>) for all synthesized molecules. The molecule benzo{c}{1,2,5}thiadiazole (BT), which acts as an electron acceptor (A) is placed between OBDT and DTP at each of the two ends of all the molecules. The number of fluorine atoms is varied on the BT core. The architecture of these molecules is based on the previous literature, which suggests that BDT with its three planar rings joined to each other can initiate considerable intermolecular interactions to develop BHJs having good charge carrier dynamics [39-42]. The BT moiety offers ease of synthesis and tuneable substitution. The DTP donor can influence the shifting of absorption maxima towards visible or NIR region [43,44].

Hence, the current work presents the synthesis of **SMD1**, **SMD2** and **SMD3** along with the interpretation of the influence of fluorine atoms on their photo-physical and electrochemical features. DFT studies are also carried out to support the experimental absorption properties. Further, we have also looked for the potential suitability of molecules **SMD1**, **SMD2** and **SMD3** to be applicable in optoelectronic devices such as OBHJSCs by means of studies of their reorganization energies, ionization potential and electron affinities by DFT methods.

# 2. Experiments

# 2.1. Materials and instruments

The chemicals utilized for the synthesis are all procured from commercial vendors and are employed without any purification processes. Experiments are performed with dry solvents (dry dichloromethane, dry toluene and dry tetrahydrofuran). Synthesized materials are characterized by NMR spectroscopy (BrukerAvance, 500 MHz) and mass spectroscopy (Thermofinngan mass spectrometer) techniques. The trends of absorption and fluorescence are measured with the help of Cary 5000 UV-Vis-NIR and Cary eclipse fluorescence spectrophotometers respectively. A PC controlled CHI 62C electrochemical analyzer was used for cyclic voltammetry studies (solvent: dichloromethane, scan rate: 100 mV/s) by taking a supporting electrolyte (0.1 M tetrabutylammonium perchlorate). The platinum wire and glassy carbon are employed as counter and working electrodes while considering the standard calomel electrode as a reference electrode (the potential of which is calibrated by adopting ferrocene as internal standard) and all the potentials are measured against standard calomel electrode. All of the above measurements are performed at room temperature (RT). Thermogravimetric experiments are carried out under nitrogen atmosphere (Exstar TG or TGA 7200, heating rate: 10 °C/min).

# 2.2. Synthetic routes

The synthetic route of **SMD1**, **SMD2** and **SMD3** are depicted in Scheme 1 and their detailed procedures are provided in the experimental section. All the molecules were prepared by following procedure from previous literature [43–46]. The target molecules of SMD1, SMD2, and SMD3 were prepared through the Stille crosscoupling reaction from distannyl intermediate 3 and their corresponding monobromo derivatives (SMD1, SMD2 and SMD3 obtained from BT-OBDT, FBT-OBDT and F2BT-OBDT respectively). The monobromo derivatives were prepared by using the Stille crosscoupling reaction pathway from their corresponding dibromo-BT derivatives (BT-OBDT, FBT-OBDT and F2BT-OBDT obtained from **BTBr<sub>2</sub>**, **FBTBr<sub>2</sub>** and **F2BTBr<sub>2</sub>** respectively) by treating with monostannyl intermediate 7. Intermediate 7 was obtained from 5 by reductive alkylation with 2-ethylhexylbromide under alkali condition followed by stannilation by using trimethylchloride in the presence of n-BuLi. The compound 5 was synthesized from commercially available thiophene-3-carboxylic acid by reacting with oxalyl chloride and 2-ethylamine followed by dimerization in the presence of n-BuLi. Intermediate 3 was synthesized from lithiation of compound **2** by using n-BuLi followed by quenching with trimethyltin chloride. Compound 2 was synthesized through dimerization of 3-bromo thiophene followed by the Buchwald-Hartwig amination pathway using 2-ethylhexylamine. All the structures of compounds were confirmed by using <sup>1</sup>H NMR, <sup>13</sup>C NMR. ESI-MS and MALDI-TOF analysis (ESI: Figs. S1-S39). The synthetic procedures of SMD1, SMD2 and SMD3 are illustrated in Scheme 1.



Fig. 1. Chemical structures of SMD1, SMD2 and SMD3.



Scheme 1. Synthetic routes for the synthesis of SMD1, SMD2 and SMD3.

2.2.1. 2,6-bis(7-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophen-2-yl)benzo[c] [1,2,5]thiadiazol-4-yl)-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (**SMD1**)

A 50 mL round bottom flask was charged with **3** (0.117 g, 0.19 mmol), **BT-OBDT** (0.375 g, 0.56 mmol) and tetrakis(-triphenylphosphine)palladium (22 mg, 0.019 mmol) followed by the addition of 20 mL of dry toluene. The reaction mixture was kept under nitrogen atmosphere for 20 min and then refluxed overnight. When the complete consumption of **3** was indicated by TLC, the reaction mixture was cooled to room temperature followed by the addition of 20 mL of chloroform. The resulting solution was passed through Celite bed and filtrate was given a workup with water and chloroform to extract compound with chloroform ( $2 \times 20$  mL). The collected organic phase was dried by adding anhydrous Na<sub>2</sub>SO<sub>4</sub> and then filtered. The filtrate was rota-vaporized and the residue was purified utilizing a column of silica gel (eluent: chloroform/petroleum ether, 4:6 v/v). **SMD1** is obtained as a blue-black solid (yield 73%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 0.97–1.04 (m, 18H), 1.06–1.13 (m, 12H),1.40–1.52 (m, 22H), 1.56–1.77 (m, 16H), 1.77–1.86, (m, 6H), 1.89–1.95 (m, 1H), 3.90–4.06 (m, 2H), 4.11–4.19 (m, 8H), 7.16 (d, J = 5.2 Hz, 2H), 7.24 (d, J = 5.5 Hz, 2H),7.43 (d, J = 6.4 Hz, 2H), 7.54 (d, J = 7.2 Hz, 2H), 7.81 (s, 2H), 8.59 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 11.24, 11.36, 14.07, 14.13, 23.01, 23.08, 23.71, 23.79, 29.09, 29.20, 30.29, 30.49, 40.51, 40.58, 75.410, 75.54, 111.69, 115.44, 119.93, 121.17, 123.23, 123.90, 125.61, 126.66, 128.36, 129.81, 131.77, 132.32, 138.30, 143.72, 144.69, 146.8, 146.66, 151.77, 152.32; MALDI-

MS (m/z): Calc. for C<sub>80</sub>H<sub>97</sub>N<sub>5</sub>O<sub>4</sub>S<sub>8</sub> is [M]<sup>+</sup>: m/z 1447.53 Found: 1447.63.

2.2.2. 2,6-bis(7-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophen-2-yl)-5-fluorobenzo[c] [1,2,5]thiadiazol-4-yl)-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (SMD2)

It is synthesized as per the procedure described for **SMD1** using **3** and **FBT-OBDT** as synthetic precursors (yield 70%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 1.01–1.06 (m, 18H), 1.08–1.14 (m, 12H), 1.44–1.52 (m, 24H), 1.60–1.74 (m, 14H), 1.77–1.83, (m, 6H), 1.95–2.01, (m, 1H), 3.92–4.04 (m, 2H), 4.08–4.14 (m, 8H), 7.04 (d, *J* = 5.2 Hz, 2H), 7.14 (d, *J* = 5.2 Hz, 2H),7.33 (d, *J* = 13.0 Hz, 2H), 7.91 (s, 2H), 8.48 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm): 11.33, 11.19, 14.10, 14.03, 22.96, 23.02, 23.59, 23.66, 29.04, 29.15, 30.15, 30.39, 40.41, 40.46, 75.02, 111.90, 117.42, 119.55, 121.88, 122.48, 125.46, 127.83, 129.38, 131.68, 136.24, 143.24, 144.39, 146.10, 148.97, 152.06, 156.26, 158.28; MALDI-MS (*m*/*z*): Calc. for C<sub>80</sub>H<sub>95</sub>F<sub>2</sub>N<sub>5</sub>O<sub>4</sub>S<sub>8</sub> is [M]<sup>+</sup>: *m*/*z* 1483.51 Found: 1483.77.

2.2.3. 2,6-bis(7-(4,8-bis((2-ethylhexyl)oxy)benzo[1,2-b:4,5-b'] dithiophen-2-yl)-5,6-difluorobenzo[c] [1,2,5]thiadiazol-4-yl)-4-(2ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (SMD3)

It is synthesized following the procedure for **SMD1** synthesis, but by using **3** and **F2BT-OBDT** as precursors (yield 76%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm): 1.01–1.05 (m, 18H), 1.06–1.10 (m, 12H), 1.42–1.51 (m, 26H), 1.57–1.66 (m, 10H), 1.65–1.73 (m, 8H), 1.87–1.94 (m, 1H), 3.76–3.91 (m, 2H), 3.93–3.99 (m, 8H), 6.78 (d,

 $J = 50.8 \text{ Hz}, 4\text{H}, 7.57 (s, 2\text{H}), 8.14 (s, 2\text{H}): {}^{13}\text{C} \text{ NMR} (100 \text{ MHz}, \text{CDCl}_3, \delta \text{ ppm}): 10.81, 11.42, 11.57, 14.31, 23.18, 23.22, 23.87, 23.97, 28.81, 29.31, 29.4, 29.71, 30.41, 30.66, 30.70, 40.70, 40.77, 75.12, 75.30, 77.51, 109.41, 112.11, 112.20, 112.61, 112.72, 118.10, 118.27, 119.61, 123.25, 123.36, 125.71, 129.10, 129.84, 130.71, 131.10, 131.33, 131.84, 143.37, 144.67, 146.68, 147.81; MALDI-MS ($ *m/z*): Calc. for C<sub>80</sub>H<sub>93</sub>F<sub>4</sub>N<sub>5</sub>O<sub>4</sub>S<sub>8</sub> is [M]<sup>+</sup>:*m/z*1519.49 Found: 1519.34 [M]<sup>+</sup>, 1520.39 [M+H]<sup>+</sup>.

# 3. Results and discussion

# 3.1. Solution processability and thermal stability

The compounds **SMD1**, **SMD2** and **SMD3** are soluble (~25 mg/ mL) in a number of organic solvents like *o*-dichlorobenzene, chloroform, dichloromethane (DCM), tetrahydrofuran (THF), acetonitrile and toluene. This shows the ease of their solution processability.

Tough resistance to decomposition at high temperatures maps the functioning of a material to be employable in actual applications. Hence, the thermal stability of **SMD1**, **SMD2** and **SMD3** are scrutinized by TGA (thermogravimetric) analysis. The molecules **SMD1**, **SMD2** and **SMD3** showed optimum thermal toughness with T<sub>d</sub> (decomposition temperature; at which 5% weight loss occurs) of 329 °C, 320 °C and 244 °C respectively (Table 1). TGA curves for **SMD1**, **SMD2** and **SMD3** are given in Fig. 2.

#### 3.2. Photo-physical and electrochemical traits

The absorption and fluorescence features of SMD1, SMD2 and **SMD3** are measured in acetonitrile. The spectra of ultraviolet-visible absorption and emission are presented in Fig. 3a and Fig. 3b respectively and the spectral data has been shown in Table 1. In these molecules, the terminal OBDT donor is conjugated to the acceptor BT which in turn is conjugated to secondary donor DTP. This conjugation strengthens electronic coupling amid electron-donating and electron-receiving fragments of a molecule. This gives way to broad as well as high-intensity optical absorption. Absorption spectra of all three donors are alike in the way they show two broad characteristic bands with good intensity; one band in the 300–425 nm region, which arises as a result of  $\pi \rightarrow \pi^*$ excitation of electrons in the conjugated molecular framework and another in 450-750 nm region, which arises because of charge transfer within molecule (intramolecular charge transfer among the electron-donating and electron-receiving fragments of molecule).

From Table 1, it can be noticed that the wavelength of maximum

#### Table 1

The decomposition temperature (T<sub>d</sub> in °C), experimental absorption maximum ( $\lambda_{exp}$  in nm), molar extinction coefficient ( $\varepsilon$  in L M<sup>-1</sup>cm<sup>-1</sup>) and emission maximum ( $\lambda_{flu}$  in nm) of molecules **SMD1**, **SMD2** and **SMD3** recorded in CH<sub>3</sub>CN at 10<sup>-5</sup> M concentration. Cyclic voltammetry measurements are performed in 1 mM dichloromethane solution with 0.1 M of Bu<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte.

Molecule	T <sub>d</sub>	Photo-physical properties		Electrochemical properties				$\Phi^{a}_{\mathrm{f}}$	
		$\lambda_{exp}$	€	$\lambda_{\rm flu}$	Eox*	E <sup>†</sup> lumo	$E_{\text{homo}}^{\ddagger}$	$\mathrm{E}^{\ddagger}_{\mathrm{g}}$	
SMD1	329	598	$0.25  imes 10^5$	730	0.46	-3.28	-5.16	1.88	0.052
SMD2	320	557	$0.17 \times 10^5$	730	0.447	-3.29	-5.17	1.88	0.107
SMD3	244	544	$0.16 \times 10^5$	710	0.53	-3.31	-5.23	1.92	0.072

\* $E_{ox}$  is the onset potential of oxidation in Volts.<sup>‡</sup> $E_{homo} = -(5.1 + E_{ox})$  in eV.<sup>†</sup> $E_{lumo} = (E_g + E_{homo})$  ineV.<sup>†</sup> $E_{gi}$  the optical band gap in eV, which was estimated from the intersection between the absorption and emission spectra. $\Phi$ <sup>‡</sup>Fluorescence quantum yield measured in cyclo hexane, relative to 9,10-diphenyl anthracene ( $\Phi_f = 0.9$  in cyclohexane).



Fig. 2. TGA curve of molecules SMD1, SMD2 and SMD3.

absorption blue shifts as the number of fluorine atoms increase from **SMD1** to **SMD3** and it is consistent with earlier observations [7,8,21,47]. The amount of blue shift from SMD1 to SMD2 is 41 nm, while that from SMD1 to SMD3 is 54 nm. As the number of fluorine atom increases: they withdraw more electron density from highest occupied molecular orbital (HOMO) and stabilize HOMO, while lowest unoccupied molecular orbital (LUMO) levels are minimally affected by the presence/increased number of fluorine atoms. The HOMO of molecule SMD2 (having two fluorine atoms) is stabilized by 0.01 eV (Table 1) as compared to that of SMD1. The HOMO of molecule SMD3 (having four fluorine atoms) is stabilized by 0.07 eV as compared to that of SMD1. Also, the LUMO levels of SMD2 and SMD3 are stabilized by 0.01 eV and 0.03 eV respectively as compared to that of SMD1. Hence, it is clear that the increased number of fluorine atom has lowered the energies of HOMOs to a higher extent as compared to that of LUMOs. This has caused the widening of the energy gap as the number of fluorine atom increases (Table 1). This accounts for the occurrence of blue-shifted absorption maxima.

The emission properties of the molecules are measured in acetonitrile (excitation wavelength at 600 nm) and are presented in Table 1, from which it can be observed that emission maxima of the molecules SMD1, SMD2 and SMD3 are 730 nm, 730 nm and 710 nm respectively and are least affected by fluorine substitution. The quantum yields for these compounds are also measured in cyclohexane by using anthracene as standard ( $\Phi_f = 0.9$ ). The measured quantum yields for the molecules SMD1, SMD2 and SMD3 are 0.052, 0.107 and 0.072 respectively (excitation wavelength for quantum yields for the molecules SMD1, SMD2 and SMD3 are 524 nm, 511 nm and 512 nm respectively).

Cyclic voltammetry (CV) experiments are performed in order to examine electrochemical properties of **SMD1**, **SMD2** and **SMD3** and the resulting CV plots are provided in Fig. 4. The energies of frontier molecular orbitals (HOMO and LUMO) and bandgap ( $E_g$ ) of **SMD1**, **SMD2** and **SMD3**, which are derived from CV experiments can be found in Table 1. In the light of data obtained in Table 1, the energy gap of molecules vary as follows; **SMD3**>**SMD2** = **SMD1**.

# 3.3. Density functional theory (DFT) studies

The DFT and TD-DFT (time dependent density functional theory) methods are utilized for all the theoretical studies. Calculations for **SMD1**, **SMD2** and **SMD3** molecules are carried out with the help of the Gaussian16 W package [48].



Fig. 3. (a) The UV–Visible spectrum of SMD1, SMD2 and SMD3 measured at 10 μM concentration in acetonitrile, (b) The fluorescence spectrum of molecules SMD1, SMD2 and SMD3 measured in acetonitrile at 10<sup>-4</sup> M concentration.



Fig. 4. Cyclic voltammetry plots of molecules SMD1, SMD2 and SMD3 measured in 1 mM dichloromethane solution with 0.1 M of Bu<sub>4</sub>NClO<sub>4</sub> as a supporting electrolyte.

# 3.3.1. Geometry optimization

The ground-state structure optimization of molecules **SMD1**, **SMD2** and **SMD3** is accomplished by employing B3LYP functional [49,50] with a 6-31G (d, p) basis set in the gas phase. The presence of local minima on potential energy curves for each molecule as well as the absence of imaginary frequencies confirmed the stability of molecules in their ground states. Replacement of lengthy and branched alkyl groups with a simple methyl group is done in order to facilitate computational methods. The molecules **SMD1**, **SMD2** and **SMD3** are planar. The dihedral angle between each donor and acceptor is calculated to be less than 13° (Fig. S40). The front view and side view of the planar structures are provided in Fig. 5.

#### 3.3.2. Theoretical absorption properties

UV–Vis characteristics of molecules **SMD1**, **SMD2** and **SMD3** are screened by treating molecules with TD-CAM-B3LYP/6-31G (d, p) method in the gas phase. The TD-CAM-B3LYP/6-31G (d, p) method is applied on molecules optimized in their ground state in the gas phase by B3LYP functional using 6-31G (d, p) basis set. CAM-B3LYP is a hybrid functional, which is believed to yield good results of properties of organic molecules with elongated  $\pi$ -conjugation.

CAM-B3LYP [51] is the range separated functional with short-range HF exchange [Coulomb attenuated version of B3LYP (CAM-B3LYP) consisting of 19% HF exchange at short range with 65% HF exchange at long range]. The calculated absorption maxima ( $\lambda_G$ ), oscillator strength ( $f_G$ ), major electronic transitions [(MT)<sub>G</sub>] and mixing coefficient [(%C<sub>i</sub>)<sub>G</sub>] are presented in Table 2. Fig. 6 presents the normalized theoretical absorption spectrum of **SMD1**, **SMD2** and **SMD3** in the gas phase.

The experimental absorption ( $\lambda_{exp}$ ) of molecules **SMD1**, **SMD2** and **SMD3** are 598 nm, 557 nm and 544 nm (Table 1) respectively; while their theoretical absorptions are 571 nm, 532 nm and 520 nm (Table 2) respectively, which indicates a fair agreement of theoretical results with experimental ones within the limitation. The experimentally observed trend of increasing blue shift as we move from **SMD1** to **SMD3** is also followed in theoretical absorption properties.

The theoretical absorption spectrum of **SMD1**, **SMD2** and **SMD3** in the gas phase shows two absorption peaks similar to their experimental absorption spectrum. The absorption maxima with the highest oscillator strength in each molecule correspond to the major electronic transition from HOMO  $\rightarrow$  LUMO. With respect to this absorption peak, one can notice that the theoretical blue shift from **SMD1** to **SMD2** is 39 nm and that from **SMD1** to **SMD3** is 51 nm, which closely mimics the trend observed experimentally as discussed in section 3.2. The absorption maxima (with lower oscillator strength) found between 300 nm and 350 nm in each molecule corresponds to electronic transitions between different energy levels (mentioned in Table 2).

Further, computations of the wavelength of maximum absorption of **SMD1**, **SMD2** and **SMD3** in acetonitrile (Table S1) are done at the same level of theory using the IEFPCM method (Integral Equation Formalism Variant of the Polarisable Continuum Model) [52]. The calculated absorption in the acetonitrile solvent is in agreement with the experimental results (Table S1).

#### 3.3.3. Frontier molecular orbitals (FMOs)

The examination of frontier molecular orbitals is conducted to comprehend the distribution of electron density in HOMO and LUMO of molecules. The frontier molecular orbitals of the molecules **SMD1**, **SMD2** and **SMD3** are pictured at CAM-B3LYP/6-31G (d, p) level of theory (Fig. 7). From FMO analysis, it is very clear that the electron density is spread majorly on DTP donor and to a lesser extent on BDT donor in the ground state (in HOMO). Upon electronic excitation, one can see that electron density shifts majorly on acceptor BT core (in LUMO).



Fig. 5. Optimized ground state structures consisting of both front view and side view of molecules SMD1, SMD2 and SMD3 computed at B3LYP/6–31 G(d,p) level of theory in gas phase.

#### Table 2

The theoretical absorption maximum ( $\lambda_G$  in nm), oscillator strength ( $f_G$ ), major electronic transitions [ (MT)<sub>G</sub>] and mixing co-efficient in gas phase [ ( $(%C_i)_G$ ] of molecules **SMD1**, **SMD2** and **SMD3** calculated at CAM-B3LYP/6-31G (d, p) level of theory in gas phase.

Molecule	$\lambda_{G}$	$f_{\rm G}$	(MT) <sub>G</sub>	(%C <sub>i</sub> ) <sub>G</sub>
SMD1	571	2.35	$H \rightarrow L$	84.94
	327	0.86	$\text{H} \rightarrow \text{L+2}$	41.43
	342	0.25	$H-3 \rightarrow L+1$	22.01
SMD2	532	2.20	$H \rightarrow L$	86.05
	318	0.82	$H-5 \rightarrow L$	26.77
	328	0.54	$H \rightarrow L{+}2$	37.97
SMD3	520	2.33	$H \rightarrow L$	83.17
	316	0.99	$H \rightarrow L{+}2$	39.35
	325	0.24	$H-3 \rightarrow L+1$	65.45

3.3.4. Reorganization energy, ionizing potential and electron affinity

Reorganization energy ( $\lambda_{re}$ ) screens the applicability of molecules as hole or electron transport materials and also the ease of achieving a balance between electron and hole injections. In simple terms,  $\lambda_{re}$  quantifies the energy changes occurring in a system after a molecular structure relaxes on account of exceeding negative and positive charges. The Marcus theory [53,54] shows the dependence of the charge transfer rate ( $K_{ct}$ ) on reorganization energy as in equation (1).

$$K_{ct} = \left(\frac{V^2}{h}\right) \left(\frac{\pi}{\lambda_{re} T k_B}\right)^{\frac{1}{2}} \exp\left(\frac{-\lambda_{re}}{4 T k_B}\right) \tag{1}$$

In equation (1),  $k_B$ , T,  $\lambda_{re}$  and V are Boltzmann constant, temperature, reorganization energy and integral of intermolecular charge transfer respectively. It is evident from equation (1) that



Fig. 6. Calculated absorption spectrum of molecules SMD1, SMD2 and SMD3 calculated at CAM-B3LYP/6-31G(d,p) level in gas phase.

charges transfer rate is majorly dependent on  $\lambda_{re}$  and V. Reorganization energy is composed of internal and external reorganization energies. Internal reorganization energy is influenced by intramolecular vibrations, while external reorganization energy involves the impact of the surrounding medium. One can ignore the values of external reorganization energy as they are pretty lower than that of internal reorganization energies [55]. Hence, we have computed internal reorganization energies [complete internal hole reorganization energy ( $\lambda_{\rm H}$ ) and electron reorganization energy ( $\lambda_{\rm E}$ )] as shown in equation (2) and equation (3).

$$\lambda_H = \lambda_1 + \lambda_2 \tag{2}$$

$$\lambda_E = \lambda_3 + \lambda_4 \tag{3}$$

where  $\lambda_1 = E^c(g_n) - E^c(g_c)$ 

# Table 3

λ

The hole reorganization energy ( $\lambda_{\rm H}$ , in meV), electron reorganization energy ( $\lambda_{\rm F}$ , in meV), adiabatic ionization potential (IPa, in eV) and adiabatic electron affinity (EAa, in eV) of SMD1, SMD2 and SMD3 calculated at B3LYP/6-31G(d,p) level of theory.

Molecule	$\lambda_{H}$	$\lambda_{E}$	IPa	EAa
SMD1	184	167	5.54	2.10
SMD2	190	171	5.54	2.13
SMD3	175	187	5.66	2.22

$$\lambda_2 = E^n(g_c) - E^n(g_n)$$
$$\lambda_3 = E^a(g_n) - E^a(g_a)$$
$$\lambda_4 = E^n(g_a) - E^n(g_n)$$

where  $E^{n}(g_{n})$  is the energy of the neutral molecule in neutral geometry,  $E^{c/a}$  (g<sub>c/a</sub>) is energy of ion (cation/anion) in ionic(cation/ anion) geometry,  $E^{c/a}(g_n)$  is energy of ion (cation/anion) in neutral geometry and  $E^n(g_{c/a})$  is the energy of the neutral molecule in ionic (cation/anion) geometry.

From, equation (1) it is obvious that charge transfer rate and reorganization energy bear inverse relationship. Hence molecules having lesser reorganization energy possess superior charge transfer characteristics. The  $\lambda_{re}$  for molecules **SMD1**, **SMD2** and SMD3 are calculated and are presented in Table 3.

As compared to the standard hole transport material TPD [N,N'diphenyl- *N*,*N*′-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine], which exhibits  $\lambda_{\rm H} = 290 \text{ meV}$  [56]; the molecules **SMD1**, **SMD2** and **SMD3** display lower  $\lambda_{\rm H}$  values implying that they can be good hole transport materials. The order of variation of  $\lambda_{\rm H}$  is as follows: **SMD1**  $\cong$  **SMD2** > **SMD3**. Further evaluation of electron transport energies of SMD1, SMD2 and SMD3 reveals that they show lower values of  $\lambda_{\rm E}$  as compared to Alg3 [tris(8-hydroxyquinolinato)aluminum(III),  $\lambda_E = 276$  meV] [57], which is a typical electron transport material. Hence SMD1, SMD2 and SMD3 can also be better electron transport materials. The trend of  $\lambda_E$  is as follows: **SMD1**  $\cong$  **SMD2** < **SMD3**. It is concluded that the reported molecules act as both hole and electron transport materials.

The impact of fluorine substitution on hole and electron



Fig. 7. The frontier molecular orbitals of SMD1, SMD2 and SMD3 molecules as calculated at CAM-B3LYP/6-31G(d,p) level.

transport properties can be comprehended as: i) the absence of strong electron-withdrawing fluorine substitution has caused **SMD1** to show the better electron-transport property, and ii) the four fluorine atoms substituted **SMD3** molecule majorly transports charge by hole mechanism.

Since the difference between  $\lambda_H$  and  $\lambda_E$  of each of **SMD1**, **SMD2** and **SMD3** is less than 24 meV, one can expect them to strike a very good balance between the hole and electron transfer rates and act as ambipolar molecules.

To construct a competent optoelectronic device, it is necessary to verify the efficiency of the injection of electron and hole into the organic material. The factors such as ionization potential (IP) and electron affinity (EA) influence the barrier of energy for the injection of electrons and holes. Ionization potential is the energy provided to the system to take its electron away (lesser the IP greater will be the ease of injection of the hole into HOMO of the molecule). Electron affinity is the energy unleashed upon the addition of an electron to the system (higher the EA better will be the injection of an electron into LUMO of the molecule). Hence, we have calculated IP (adiabatic) and EA (adiabatic) of **SMD1**, **SMD2** and **SMD3** at B3LYP/6-31G (d, p) level of theory and the result are shown in Table 3, from which we can comprehend that **SMD1**, **SMD2** and **SMD3** have sufficiently lower values of IP and higher values of EA; so that they can be employed in organic electronic materials.

The trend of variation of IP and EA both, which are influenced by fluorine atom inclusion, is as follows: **SMD1**  $\cong$  **SMD2** < **SMD3**. The incorporation of four strongly electron-accepting fluorine atoms has increased the difficulty of removing an electron from **SMD3** by 0.12 eV as compared to **SMD1** (which has no fluorine substitution), while the same electron attracting tendency of **SMD3** has resulted in increasing values of EA by 0.12 eV as compared to **SMD1**. The influence of two fluorine atoms in **SMD2** seems to be minimum and its EA and IP values are very close to those of **SMD1**.

#### 4. Conclusions

Three organic molecules SMD1, SMD2 and SMD3 having D<sub>I</sub>-A- $D_{II}$ -A- $D_I$  type architecture are synthesized. The molecules **SMD1**, SMD2 and SMD3 bear 0, 2 and 4 fluorine atoms respectively, which are substituted on their acceptor core. The influence casted by fluorine atoms on the photo-physical and electrochemical traits of molecules is investigated by means studies of electronic excitations and cyclic voltammetry. And also, DFT methods helped in appreciating the influence of fluorine atoms on reorganization energies, ionization potential and electron affinity of molecules. The major influence of fluorine atoms on properties of molecules presented in this work can be pointed out as: (a) as number of fluorine atom increases, there will be more withdrawal of electron density from HOMOs and hence HOMO levels of molecules go on deepening as number of fluorine atom increases, (b) the LUMOs of molecules are not affected significantly by fluorine substitution, (c) increasing fluorine substitution has increased the HOMO-LUMO gap (SMD1 < SMD2 < SMD3) and has resulted in increased magnitudes of blue shift, (d) studied molecules are with low reorganization energies and are considered as better hole and electron transport materials. Since the difference between  $\lambda_{\rm H}$  and  $\lambda_{\rm E}$  of each of **SMD1**, SMD2 and SMD3 is less than 24 meV, they can act as ambipolar molecules.

Additionally, the solution processability and thermal stability of the synthesized materials make them desirable in device fabrication. They have good molar extinction co-efficient to use them in solar cells to harvest solar energy and the broad and NIR region absorption of all three molecules can upgrade the exciton generating capability and short circuit current density (J<sub>SC</sub>) of the OBHJSCs. Hence, this combined experimental and DFT study points towards the possibilities of applicability of molecules **SMD1**, **SMD2** and **SMD3** in the construction of OBHJSCs and in organic electronic materials.

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## **Declaration of competing interest**

No conflict of interest exists. We wish to confirm that there are no known conflicts of interest associated with this publication and there has been no significant financial support for this work that could have influenced its outcome.

# **CRediT** authorship contribution statement

**Ejjurothu Appalanaidu:** Methodology, Data curation, Formal analysis, Writing - review & editing. **V.M. Vidya:** Formal analysis, Writing - original draft, Writing - review & editing. **Manohar Reddy Busireddy:** Methodology, Data curation, Formal analysis, Writing - review & editing. **Jayathirtha Rao Vaidya:** Conceptualization, Formal analysis, Resources, Writing - review & editing. **Prabhakar Chetti:** Software, Supervision, Validation, Visualization, Formal analysis, Writing - original draft, Writing - review & editing.

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## Appendix A. Supplementary data

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# References

- [1] H. Bin, Y. Yang, Z.-G. Zhang, L. Ye, M. Ghasemi, S. Chen, Y. Zhang, C. Zhang, C. Sun, L. Xue, C. Yang, H. Ade, Y. Li, 9.73% efficiency non-fullerene all organic small molecule solar cells with absorption-complementary donor and acceptor, J. Am. Chem. Soc. 139 (2017) 5085–5094, https://doi.org/10.1021/ jacs.6b12826.
- [2] J.R. Tumbleston, B.A. Collins, L. Yang, A.C. Stuart, E. Gann, W. Ma, W. You, H. Ade, The influence of molecular orientation on organic bulk heterojunction solar cells, Nat. Photon. 8 (2014) 385–391, https://doi.org/10.1038/ nphoton.2014.55.
- [3] M.C. Scharber, D. Muehlbacher, M. Koppe, P. Denk, C. Waldauf, A.J. Heeger, C.J. Brabec, Design rules for donors in bulk-heterojunction solar cells-towards 10 % energy-conversion efficiency, Adv. Mater. 18 (2006) 789–794, https:// doi.org/10.1002/adma.200501717.
- [4] Y. Huang, E.J. Kramer, A.J. Heeger, G.C. Bazan, Bulk heterojunction solar cells: morphology and performance relationships, Chem. Rev. 114 (2014) 7006–7043, https://doi.org/10.1021/cr400353v.
- [5] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, Polymer solar cells with enhanced open-circuit voltage and efficiency, Nat. Photon. 3 (2009) 649–653, https://doi.org/10.1038/nphoton.2009.192.
- [6] K. Vandewal, K. Tvingstedt, A. Gadisa, O. Inganaes, J.V. Manca, On the origin of the open-circuit voltage of polymer-fullerene solar cells, Nat. Mater. 8 (2009) 904–909, https://doi.org/10.1038/nmat2548.
- [7] H.S. Lee, H.G. Song, H. Jung, M.H. Kim, C. Cho, J.-Y. Lee, S. Park, H.J. Son, H.-J. Yun, S.-K. Kwon, Y.-H. Kim, B. Kim, Effects of backbone planarity and tightly packed alkyl chains in the donor-acceptor polymers for high photostability, Macromolecules 49 (2016) 7844–7856, https://doi.org/10.1021/ acs.macromol.6b01580.
- [8] J.-L. Wang, Q.-R. Yin, J.-S. Miao, Z. Wu, Z.-F. Chang, Y. Cao, R.-B. Zhang,

J.Y. Wang, H.-B. Wu, Y. Cao, Rational design of small molecular donor for solution-processed organic photovoltaics with 8.1% efficiency and high fill factor via multiple fluorine substituents and thiophene bridge, Adv. Funct. Mater. 25 (2015) 3514–3523, https://doi.org/10.1002/adfm.201500190.

- [9] J. Kim, M.H. Yun, G.-H. Kim, J. Lee, S.M. Lee, S.-J. Ko, Y. Kim, G.K. Dutta, M. Moon, S.Y. Park, D.S. Kim, J.Y. Kim, C. Yang, Synthesis of PCDTBT-based fluorinated polymers for high OpenCircuit voltage in organic photovoltaics: towards an understanding of relationships between polymer energy levels engineering and ideal morphology control, ACS. Appl. Mater. 6 (2014) 7523–7534, https://doi.org/10.1021/am500891z.
- [10] J. Lee, M. Jang, S.M. Lee, D. Yoo, T.J. Shin, J.H. Oh, C. Yang, Fluorinated benzothiadiazole (BT) groups as a powerful unit for high-performance electrontransporting polymers, ACS. Appl. Mater. 6 (2014), https://doi.org/10.1021/ am505925w, 20390-2039920391.
- [11] Z. Li, J. Lu, S.-C. Tse, J. Zhou, X. Du, Y. Tao, J. Ding, Synthesis and applications of difluorobenzothiadiazole based conjugated polymers for organic photovoltaics, J. Mater. Chem. 21 (2011) 3226–3233, https://doi.org/10.1039/ C0JM04166A.
- [12] Y. Zhang, S.-C. Chien, K.-S. Chen, H.-L. Yip, Y. Sun, J.A. Davies, F.-C. Chen, A.K.-Y. Jen, Increased open circuit voltage in fluorinated benzothiadiazole-based alternating conjugated polymers, Chem. Commun. (J. Chem. Soc. Sect. D) 47 (2011) 11026–11028, https://doi.org/10.1039/C1CC14586].
- [13] L. Cartwright, A. Iraqi, Y. Zhang, T. Wang, D.G. Lidzey, Impact of fluorine substitution upon the photovoltaic properties of benzothiadiazolefluorene alternate copolymers, RSC Adv. 5 (2015) 46386–46394, https://doi.org/ 10.1039/C5RA06076A.
- [14] H. Bronstein, J.M. Frost, A. Hadipour, Y. Kim, C.B. Nielsen, R.S. Ashraf, B.P. Rand, S. Watkins, I. McCulloch, Effect of fluorination on the properties of a donoracceptor copolymer for use in photovoltaic cells and transistors, Chem. Mater. 25 (2013) 277–285, https://doi.org/10.1021/cm301910t.
- [15] S. Albrecht, S. Janietz, W. Schindler, J. Frisch, J. Kurpiers, J. Kniepert, S. Inal, P. Pingel, K. Fostiropoulos, N. Koch, D. Neher, Fluorinated copolymer PCPDTBT with enhanced open-circuit voltage and reduced recombination for highly efficient polymer solar cells, J. Am. Chem. Soc. 134 (2012) 14932–14944, https://doi.org/10.1021/ja305039j.
- [16] N. Wang, Z. Chen, W. Wei, Z. Jiang, Fluorinated benzothiadiazole-based conjugated polymers for high-performance polymer solar cells without any processing additives or post-treatments, J. Am. Chem. Soc. 135 (2013) 17060–17068, https://doi.org/10.1021/ja409881g.
- [17] J.-L. Wang, K.-K. Liu, J. Yan, Z. Wu, F. Liu, F. Xiao, Z.-F. Chang, H.-B. Wu, Y. Cao, T.P. Russell, Series of multifluorine substituted oligomers for organic solar cellswith efficiency over 9% and fill factor of 0.77 by CombinationThermal and solvent vapor annealing, J. Am. Chem. Soc. 138 (2016) 7687–7697, https:// doi.org/10.1021/jacs.6b03495.
- [18] S. Paek, N. Cho, K. Song, M.-J. Jun, J.K. Lee, J. Ko, Efficient organic semiconductors containing fluorine-substituted benzothiadiazole for solutionprocessed small molecule organic solar cells, J. Phys. Chem. C 116 (2012) 23205–23213, https://doi.org/10.1021/jp305989g.
- [19] X. Liao, F. Wua, L. Chen, Y. Chena, Solution-Processed small molecules based on benzodithiophene and difluorobenzothiadiazole for inverted organic solar cells, Polym. Chem. 6 (2015) 7726–7736, https://doi.org/10.1039/ C5PY01051A.
- [20] Y. Zhang, J. Zou, C.-C. Cheuh, H.-L. Yip, A.K.-Y. Jen, Significant improved performance of photovoltaic cells made from a partially fluorinated cyclopentadithiophene/BenzothiadiazoleConjugated polymer, Macromolecules 45 (2012) 5427–5435, https://doi.org/10.1021/ma3009178.
- [21] J.W. Jo, J.W. Jung, E.H. Jung, H. Ahn, T.J. Shin, W.H. Jo, Fluorination on both D and A Unit in D-A Type conjugated copolymers based on difluorobithiophene and benzothiadiazole for high efficient polymer solar cells, energy, Environ. Sci. 8 (2015) 2427–2434, https://doi.org/10.1039/C5EE00855G.
- [22] Y.-X. Xu, C.-C. Chueh, H.-L. Yip, F.-Z. Ding, Y.-X. Li, C.-Z. Li, X. Li, W.-C. Chen, A.K.-Y. Jen, Improved charge transport and absorption coefficient in indacenodithieno[3,2-B]Thiophene-Based ladder-type polymer leading to highly efficient polymer solar cells, Adv. Mater. 24 (2012) 6356–6361, https:// doi.org/10.1002/adma.201203246.
- [23] C.D. Dimitrakopoulos, P.R.L. Malenfant, Organic thin film transistors for large area electronics, Adv. Mater. 14 (2002) 99–117, https://doi.org/10.1002/1521-4095(20020116)14:2<99::AID-ADMA99>30.CO, 2-9.
- [24] A. Facchetti, M. Mushrush, M.-H. Yoon, G.R. Hutchison, M.A. Ratner, T.J. Marks, Building blocks for n-type molecular and polymeric electronics. Perfluoroalkyl- versus alkyl-functionalized oligothiophenes (nT; n = 2-6). Systematics of thin film microstructure, semiconductor performance, and modeling of majority charge injection in field-effect transistors, J. Am. Chem. Soc. 126 (2004) 13859–13874, https://doi.org/10.1021/ja0489846.
- [25] A. Facchetti, M.-H. Yoon, C.L. Stern, H.E. Katz, T.J. Marks, Building blocks for ntype organic electronics: regiochemically modulated inversion of majority carrier sign in perfluoroarene- modified polythiophene semiconductors, Angew. Chem. Int. Ed. 42 (2003) 3900–3903, https://doi.org/10.1002/ anie.200351253.
- [26] S.B. Heidenhain, Y. Sakamoto, T. Suzuki, A. Miura, H. Fujikawa, T. Mori, S. Tokito, Y. Taga, Perfluorinated oligo(P-phenylene)S: efficient n-type semiconductors for organic light-emitting diodes, J. Am. Chem. Soc. 122 (2000) 10240–10241, https://doi.org/10.1021/ja0023090.
- [27] B.A. Jones, A. Facchetti, M.R. Wasielewski, T.J. Marks, Tuning orbital energetics in arylene diimide semiconductors. Materials design for ambient stability of

N-type charge transport, J. Am. Chem. Soc. 129 (2007) 15259–15278, https://doi.org/10.1021/ja075242e.

- [28] H. Sirringhaus, N. Tessler, R.H. Friend, Integrated optoelectronic devices based on conjugated polymers, Science 280 (1998) 1741–1744, https://doi.org/ 10.1126/science.280.5370.1741.
- [29] J.R. Tumbleston, A.C. Stuart, E. Gann, W. You, H. Ade, Fluorinated polymer yields high organic solar cell performance for a Wide range of morphologies, Adv. Funct. Mater. 23 (2013) 3463–3470, https://doi.org/10.1002/ adfm.201300093.
- [30] A.C. Stuart, J.R. Tumbleston, H. Zhou, W. Li, S. Liu, H. Ade, W. You, Fluorine substituents reduce charge recombination and drive structure and morphology development in polymer solar cells, J. Am. Chem. Soc. 135 (2013) 1806–1815, https://doi.org/10.1021/ja309289u.
- [31] B.C. Schroeder, R.S. Ashraf, S. Thomas, A.J.P. White, L. Biniek, C.B. Nielsen, W.M. Zhang, Z.G. Huang, P.S. Tuladhar, S.E. Watkins, T.D. Anthopoulos, J.R. Durrant, I. McCulloch, Synthesis of novel thieno 3,2-b-Thienobis(Silolothiophene)-Based low bandgap polymers for organic photovoltaics, Chem. Commun. 48 (2012) 7699–7701, https://doi.org/10.1039/C2CC33718E.
- [32] B.C. Schroeder, Z.G. Huang, R.S. Ashraf, J. Smith, P. D'Angelo, S.E. Watkins, T.D. Anthopoulos, J.R. Durrant, I. McCulloch, Silaindacenodithiophene-based low band gap polymers-the effect of fluorine substitution on device performances and film morphologies, Adv. Funct. Mater. 22 (2012) 1663–1670, https://doi.org/10.1002/adfm.201102941.
- [33] Z. Li, J.P. Lu, S.C. Tse, J.Y. Zhou, X.M. Du, Y. Tao, J.F. Ding, Synthesis and applications of difluorobenzothiadiazole based conjugated polymers for organic photovoltaics, J. Mater. Chem. 21 (2011) 3226–3233, https://doi.org/10.1039/C0JM04166A.
- [34] Y.Y. Liang, Z. Xu, J.B. Xia, S.T. Tsai, Y. Wu, G. Li, C. Ray, L.P. Yu, For the bright future-bulk heterojunction polymer solar cells with power conversion efficiency of 7.4%, Adv. Mater. 22 (2010) E135–E138, https://doi.org/10.1002/ adma.200903528.
- [35] H.J. Son, W. Wang, T. Xu, Y.Y. Liang, Y.E. Wu, G. Li, L.P. Yu, Synthesis of fluorinated polythienothiophene-Co-benzodithiophenes and effect of fluorination on the photovoltaic properties, J. Am. Chem. Soc. 133 (2011), https://doi.org/ 10.1021/ja108601g, 1885–1894.
- [36] S.C. Price, A.C. Stuart, L.Q. Yang, H.X. Zhou, W. You, Fluorine substituted conjugated polymer of medium band gap yields 7% efficiency in Polymer–Fullerene solar cells, J. Am. Chem. Soc. 133 (2011) 4625–4631, https://doi.org/10.1021/ja1112595.
- [37] J.H. Park, E.H. Jung, J.W. Jung, W.H. Jo, A fluorinated phenylene unit as a building block for high-performance n-type semiconducting polymer, Adv. Mater. 25 (2013) 2583–2588, https://doi.org/10.1002/adma.201205320.
- [38] Y. Wang, X. Xin, Y. Lu, T. Xiao, X. Xu, N. Zhao, X. Hu, B.S. Ong, S.C. Ng, Substituent effects on physical and photovoltaic properties of 5,6-Difluorobenzo [c][1,2,5]thiadiazole-Based D-A polymers: toward a donor design for high performance polymer solar cells, Macromolecules 46 (2013) 9587–9592, https://doi.org/10.1021/ma401709r.
- [39] J. Yuan, X. Huang, F. Zhang, J. Lu, Z. Zhai, C. Di, Z. Jiang, W. Ma, Design of benzodithiophene-diketopyrrolopyrrole based donor-acceptor copolymers for efficient organic field effect transistors and polymer solar cells, J. Mater. Chem. 22 (2012) 22734–22742, https://doi.org/10.1039/C2JM34004F.
- [40] H. Zhou, L. Yang, A.C. Stuart, S.C. Price, S. Liu, W. You, Development of fluorinated benzothiadiazole as a structural unit for a polymer solar cell of 7 % efficiency, Angew. Chem. 50 (2011) 2995–2998, https://doi.org/10.1002/ anie.201005451.
- [41] Y. Liu, X. Wan, F. Wang, J. Zhou, G. Long, J. Tian, Y. Chen, High-performance solar cells using a solution-processed small molecule containing benzodithiophene unit, Adv. Mater. 23 (2011) 5387–5391, https://doi.org/10.1002/ adma.201102790.
- [42] S. Shen, P. Jiang, C. He, J. Zhang, P. Shen, Y. Zhang, Y. Yi, Z. Zhang, Z. Li, Y. Li, Solution-Processable organic molecule photovoltaic materials with bithienylbenzodithiophene central unit and indenedione end groups, Chem. Mater. 25 (2013) 2274–2281, https://doi.org/10.1021/cm400782q.
- [43] M.R. Busireddy, V.N.R. Mantena, N.R. Chereddy, B. Shanigaram, B. Kotamarthi, S. Biswas, G.D. Sharma, J.R. Vaidya, Dithienopyrrole-benzodithiophene based donor materials for small molecular BHJSCs: impact of side chain and annealing treatment on their photovoltaic properties, Org. Electron. 37 (2016) 312–325, https://doi.org/10.1016/j.orgel.2016.07.003.
- [44] M.R. Busireddy, V.N.R. Mantena, N.R. Chereddy, B. Shanigaram, B. Kotamarthi, S. Biswas, G.D. Sharma, J.R. Vaidya, A dithieno[3,2-b:2',3'-d]pyrrole based, NIR absorbing, solution processable, small molecule donor for efficient bulk heterojunction solar cells, Phys. Chem. Chem. Phys. 18 (2016) 32096–32106, https://doi.org/10.1039/c6cp06304g.
- [45] M.R. Busireddy, V. Mantena, N.R. Chereddy, B. Shanigaram, B. Kotamarthi, S. Biswas, G.D. Sharma, J.R. Vaidya, Dithieno[3,2-b:2',3'-d]pyrrole-benzo[c] [1,2,5]thiadiazole conjugate small molecule donors: effect of fluorine content on their photovoltaic properties, Phys. Chem. Chem. Phys. 19 (2017) 20513–20522, https://doi.org/10.1039/C7CP02729].
- [46] M.R. Busireddy, C. Madhu, N.R. Chereddy, E. Appalanaidu, G. Sharma, J.R. Vaidya, Optimization of the donor material structure and processing conditions to obtain efficient small-molecule donors for bulk heterojunction solar cells, Chem. Photo. Chem. 1 (2017) 1–9, https://doi.org/10.1002/ cptc.201700170.
- [47] X. Liu, Y. Sun, B.B.Y. Hsu, A. Lorbach, L. Qi, A.J. Heeger, G.C. Bazan, Design and properties of intermediate-sized narrow band-gap conjugated molecules

relevant to solution-processed organic solar cells, J. Am. Chem. Soc. 136 (2014), https://doi.org/10.1021/ja413144u.

- [48] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, GAUSSIAN 16 (Revision B.01), Gaussian, Inc., Wallingford CT, 2016.
- [49] A.D. Becke, Density-functional exchange-energy approximation with correct asymptotic behavior, Phys. Rev. 38 (1988) 3098–3100, https://doi.org/ 10.1103/PhysRevA.38.3098.
- [50] C. Lee, W. Yang, R.G. Parr, Development of the Colle-Salvetti correlation-energy formula into functional of the electron density, Phys. Rev. B 37 (1988) 785-789, https://doi.org/10.1103/PhysRevB.37.785.

- [51] T. Yanai, D.P. Tew, N.C. Handy, A new hybrid exchange correlation functional using the Coulomb-attenuating method (CAM-B3LYP), Chem. Phys. Lett. 393 (2004) 51–57, https://doi.org/10.1016/j.cplett.2004.06.011.
- [52] J. Tomasi, B. Mennucci, R. Cammi, Quantum mechanical Continuum models, Chem. Rev. 105 (2005) 2999–3094, https://doi.org/10.1021/cr9904009.
- [53] R.A. Marcus, Electron transfer reactions in chemistry, Theory and experiment, Rev. Mod. Phys. 65 (1993) 599-610, https://doi.org/10.1103/ RevModPhys.65.599.
- [54] R.A. Marcus, H. Eyring, Chemical and electrochemical electron-transfer theory, Annu. Rev. Phys. Chem. 15 (1964) 155–196, https://doi.org/10.1146/ annurev.pc.15.100164.001103.
- [55] D.P. McMahon, A. Troisi, Evaluation of the external reorganization energy of polyacenes, J. Phys. Chem. Lett. 1 (2010) 941–946, https://doi.org/10.1021/ jz1001049.
- [56] M. Malagoli, J.L. Bredas, Density functional theory study of the geometric structure and energetics of triphenylamine-based hole-transporting molecules, Chem. Phys. Lett. 327 (2000) 13–17, https://doi.org/10.1016/S0009-2614(00)00757-0.
- [57] B.C. Lin, C.P. Cheng, Z.Q. You, C.P. Hsu, Charge transport properties of tris(8hydroxyquinolinato)aluminum(III): why it is an electron transporter, J. Am. Chem. Soc. 127 (2005) 66–67, https://doi.org/10.1021/ja045087t.