

Polymer solar cells: design of materials by donor–acceptor approach

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A brief overview of our group research activities is given and the concept of donor–acceptor is described for the development of conjugated polymers for optoelectronic devices. In particular, a new family of conjugated polymers based on dithienopyrrole has been synthesized to demonstrate the concept of donor–acceptor. The dithienopyrrole was coupled to benzodithiophene via Stille coupling to obtain two low band gap polymers P5a and P5b having $-C_{18}H_{37}$ and -2 -ethylhexyl alkyl chain respectively. Both the polymers exhibit absorption within the solar spectrum with an optical band gap below 2 eV. Atomic force microscopy revealed that both the polymers form smooth film with roughness of 2.4 nm and photoluminescence measurement of polymer/fullerene derivative blend film suggests effective dissociation of exciton.

Keywords: Benzodithiophene, dithienopyrrole, donor acceptor polymers, organic photovoltaics,

Organic solar cells

SOLAR cells or photovoltaics (PVs) are devices which are capable of capturing and converting solar energy directly to electricity. Organic solar cell device contains an active layer, with appropriate band gap, upon absorbing sunlight generates an electron-hole pair (excitons) in active layer, which later diffuses to donor–acceptor interface for charge separation. The separated electron and hole charge carriers migrate to their respective electrodes, complete circuit and generate electricity. Every step of the entire process is important and adds to the overall device efficiency. An efficiency of at least 10% is necessary for organic solar cells to establish a commercial market. Presently, silicon-based solar cells are commercially available, although these devices have reached a theoretical limit of efficiency, which is known as Shockley–Queisser limit¹. Although these cells are highly efficient in energy-conversion process, their production cost is prohibitive². Thin film is another outlook for harnessing solar energy using multi-junction of doped materials of Cd, Te, In, Ga, etc. Efficiency of 30–40% has been achieved in thin film solar cells; however they pose serious environmental concerns³. The major challenges are to

reduce the cost/watt and improve the efficiency. Hence new technologies like organic solar cells (OSC)/organic photovoltaics (OPVs)⁴, dye sensitized solar cells (DSSC)⁵, quantum dots⁶, etc. are emerging in this domain which give flexibility to address drawbacks concerning the available technology.

OPVs devices contain conjugated organic molecules or polymers as light absorbing active layers. As the materials used in these devices possess high solubility in common organic solvents, they can be easily solution processed over a large surface area by cost effective methods such as coating and ink-jet printing⁷. This ease of process ability reduces their production cost and has emerged as a low cost potential technology for producing roll-to-roll cost effective solar panels⁸. However, due to various problems such as partial absorption in solar spectrum, charge recombination losses at donor–acceptor interface and low dielectric constant of organic materials the excitonic charge separation is ineffective, this accounts to marginal performance and low efficiency of devices. Maximum reported efficiency of OPV devices is below 10% and these are yet to be commercialized. Different design strategies have been adopted to synthesize novel molecules to overcome their inherent shortcomings, among them the donor–acceptor (D–A) or donor–acceptor–donor (D–A–D) based approach has been widely exploited. In this method a judicious choice of electron acceptor and electron donor is made and coupled to generate D–A or D–A–D type architecture. It is expected that this kind of arrangement in materials would absorb large breadth of solar spectrum, reduces band gap, enhances exciton charge separation and charge mobility. The materials obtained by this approach would have reduced band gap (< 2 eV) and are known as low band gap organic semiconductors; in other words the material which absorbs light with wavelengths (λ) longer than 600 nm belongs to this family. D–A type low band gap materials are used as a donor in the OPV devices and chemically modified phenyl-C61/71-butyric acid methyl ester (C₆₀PCBM and C₇₀PCBM) are being widely used as acceptors because of their high electron affinity and excellent electron mobilities⁹. For enhancing charge carrier mobility and to aid exciton separation at the interface, a novel concept of bulk heterojunction (BHJ) has been widely used. In BHJ, a thin film of conjugated polymer and fullerene derivatives is prepared by intimately mixing

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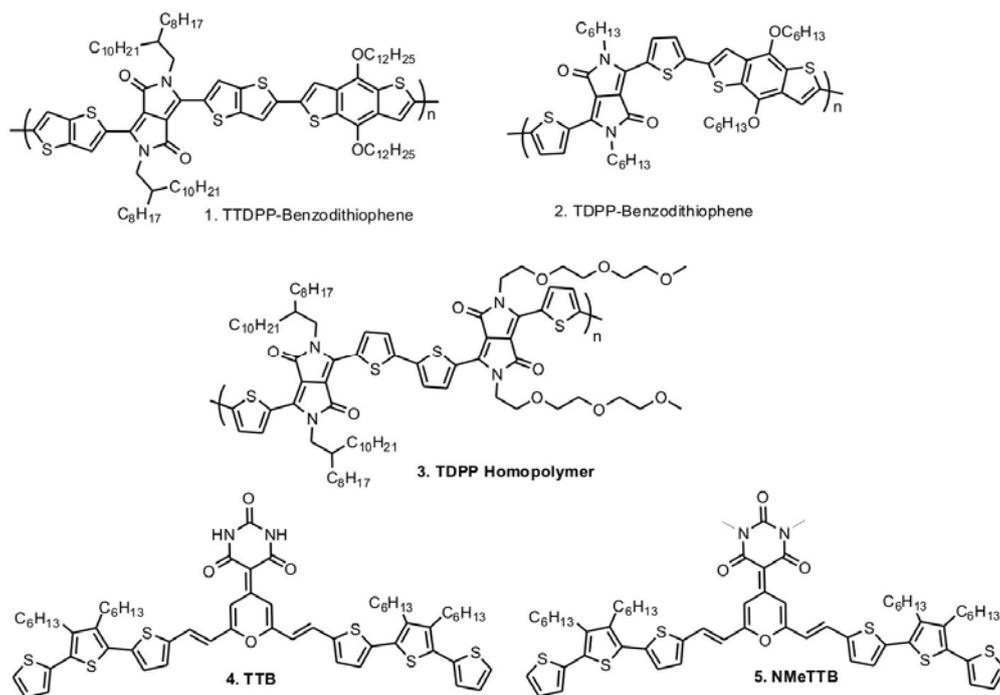


Figure 1. Different low band gap polymers/oligomers synthesized.

both the components. The donor and acceptor form interpenetrating network with spinodal decomposition drive phase separation which leads to bicontinuous network to have a percolation path for charge carriers (electrons and holes) towards electrodes.

Since the inception of D–A–D and BHJ concepts, there has been a tremendous growth in OPVs and produced device with power conversion efficiencies up to 9.8% (ref. 10). Many examples of low band gap polymers have been described in the literature^{11–16}. In recent times, the major focus of various research groups lies in using diketopyrrolopyrrole (DPP) as D–A–D central core^{17–20}. This electron-deficient planar fused core when combined with electron-rich units such as phenyl, thiophene and other aromatic heterocycles generated a library of compounds with D–A and D–A–D type arrangement. Our research group has developed materials based on DPP core and contributed significantly to organic electronics research^{13,21,22}. We synthesized thienothiopyrrole-DPP (TTDPP) and coupled with benzodithiophene to obtain polymer TTDPP-benzodithiophene (Figure 1) and obtained a device with 3.26% efficiency, similarly when the polymer was used in inverted cell an efficiency of 4.3% was recorded (Figure 2a). In another study, we coupled thiophene DPP (TDPP) with benzodithiophene and obtained efficiency of 2.7% (ref. 13).

Recently, our group has reported synthesis of a homopolymer of TDPP with alternating different alkyl chains and achieved electron mobility of $3.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Figure 2b)²¹. In the BHJ solar cells, one of the major issues is phase separation between donor and acceptor units which

leads to phase separation and instability and to address this issue, we have developed supramolecular materials (TTB and NMeTTB). These materials are capable of forming intermolecular H-bonding interactions within itself and with acceptors²². Preliminary results indicate that, indeed, phase separation can be addressed by using supramolecular concepts²³.

In the present work, we report synthesis and photophysical studies of D–A type copolymer containing fused aromatic planar rings, i.e., dithienopyrrole (DTP) and benzodithiophene (BDT). DTP is an aromatic unit containing a pyrrole fused with two thiophenes, forming a planar tricyclic system with excellent crystalline structure and showing good π -conjugation. Due to its low ionization potential, it can easily oxidize and remain oxidized for a longer period, making it an excellent electron donor. It has been studied that *N*-substitution with alkyl chains for solubility has minimum impact on the polymer electronic properties. The system by design contains fused thiophenes with a pyrrole ring would generate electron-rich derivative and subsequently; coupling with electron deficient systems D–A or D–A–D type structures with low band gap can be generated. With this ideology, many low band gap polymers of DTP have been synthesized and studied for organic electronic applications. Rasmussen and co-workers^{24–26} synthesized and used DTP-based materials for organic electronic applications. Later, Liu *et al.*²⁷ reported that less ordered and as-cast films of DTPs gave high carrier mobility in comparison to the ordered ones. This typical behaviour of DTPs was ascribed to backbone-to-backbone contact which assisted in effective

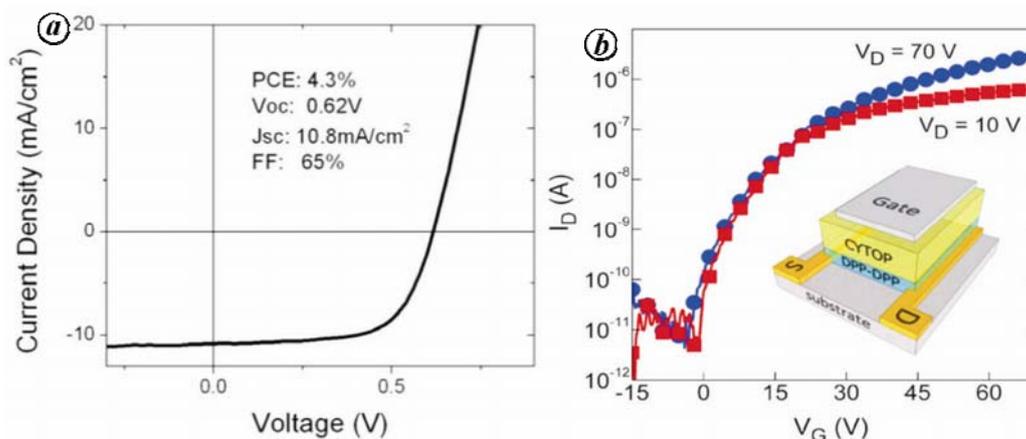


Figure 2. *a*, I–V Characteristics of inverted device architecture for TTDPP-benzothiadiazole based polymer; *b*, Transfer characteristics of top gate bottom contact transistor for TDPP homopolymer.

interchain hopping. Zhan *et al.*²⁸ used the DTP-based polymer in all polymer solar cell and recorded an efficiency of 1.5%; in another study using DTP-based polymers Price *et al.*²⁹ recorded an efficiency of 1%. Gong *et al.*³⁰, while studying the effect of alkyl chains found longer alkyl chain on DTP polymer that gave an efficiency of 1.1%, which was higher in comparison to the one with small alkyl chain. Despite constant efforts in structure and device optimization, the low efficiency of DTP polymers has not made an impact on the photovoltaic research. The main reason is due to high lying highest occupied molecular orbitals (HOMO) level which gives low V_{oc} (open circuit voltage) when blended along with phenyl-C61-butyric acid methyl ester (PCBM). In this regard, we find an enormous opportunity in optimizing the structure and coupling with other electron-deficient systems to generate polymers with low band gap and use these materials in solar cells. Here, we report our first attempt of modification of DTP energy level by generating new family of conjugated polymers.

Experimental section

Materials

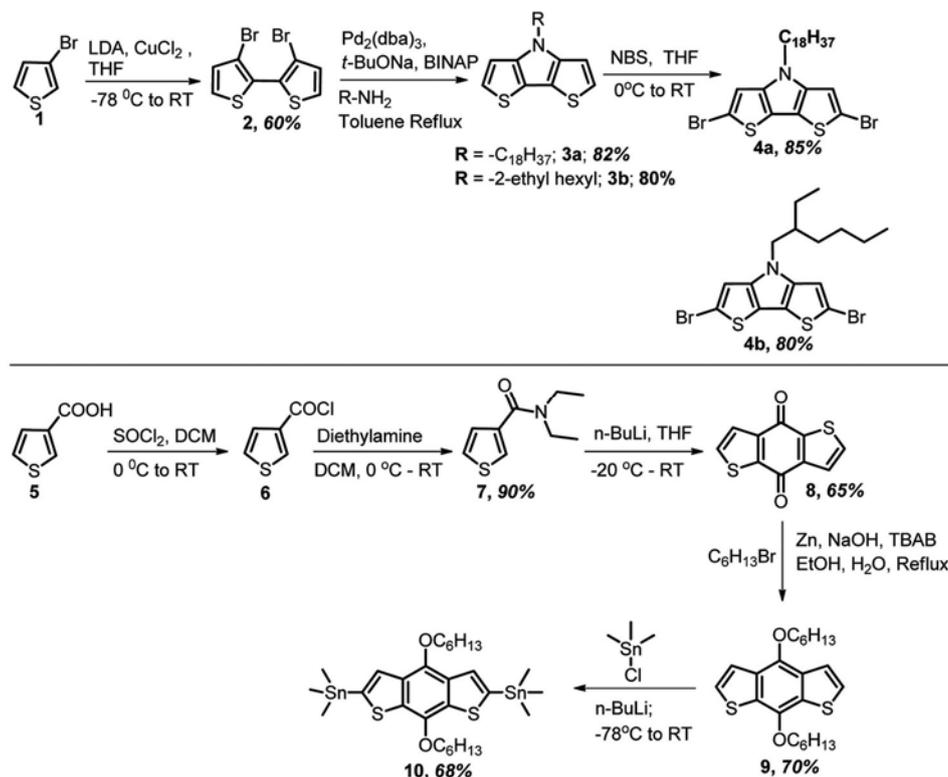
All reagents (AR grade) were purchased from S.D. Fine Chemicals, Spectrochem, Sigma-Aldrich and were used as supplied unless otherwise stated. All solvents for reactions were distilled once. All reactions were performed in oven dried apparatus and were stirred magnetically. (4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole) (**3b**) and (2,6-dibromo-4-(2-ethylhexyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole) (**4b**) were synthesized according to the reported literature procedures³¹. (4,8-Bis(hexyloxy)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl)bis(trimethyl stannane) (**10**) was synthesized according to previous reported procedures^{11,13,32} (Scheme 1).

Characterization

¹H and ¹³C NMR spectra were recorded on a Bruker 400 MHz (100 MHz ¹³C) NMR spectrometer and calibrated using TMS as an internal reference. Chemical shifts are reported in parts per million (ppm) and multiplicity is indicated using the following abbreviations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), sb (broad singlet) and db (broad doublet). The UV-vis-spectra were recorded on Perkin-Elmer (Lambda 35) UV-visible spectrometer. All the spectra in solution were recorded in CHCl₃ (conc. 1×10^{-5} mol/l) and the spectra in the solid state were recorded from films of compounds spin coated on quartz substrate. Steady-state fluorescence emission studies were carried out with Spectro Fluoro-Log-3 fluorometer (Jobin-Yvon Inc.). Cyclic voltammetry was carried out on CHI 400 Instrument using a three-electrode cell. Platinum wire was used as the counter electrode. The platinum rod electrode coated with a thin film layer of polymers was used as working electrode. Ag/Ag electrode (Ag in a 0.01 mol/l AgNO₃) was used as the reference electrode, calibrated against the Fc/Fc couple (0.09 V versus Ag/Ag) at the beginning of the experiment. Anhydrous and nitrogen-saturated solution of 0.1 M of tetrabutylammonium hexafluorophosphate (*n*-Bu₄NPF₆) in acetonitrile was employed as the supporting electrolyte. Atomic force microscopy (AFM) was carried out in tapping mode using Bruker 5500 AFM. Films were prepared on the silicon substrate by spin coating from 10 mg/ml solution of the polymers in *o*-dichlorobenzene and dried at 50°C for 10 min.

Synthesis

3,3'-Dibromo-2,2'-bithiophene (2): In a 500 ml round bottom flask, 3-bromothiophene (10.0 g, 61.35 mmol) was taken with anhydrous THF (100 ml). The solution was cooled to -78°C and LDA (38.4 ml, 1.6 M solution)



Scheme 1. Synthesis strategy for monomers **4a**, **4b** and **10**.

was added drop wise over 15 min. After the addition, the solution was stirred at the same temperature for 1 h and CuCl_2 (16.4 g, 122.70 mmol) was added in portion. The mixture was then allowed to stir at -78°C for 1 h and then at room temperature for 5 h. The reaction was quenched with 200 ml of water. The compound was extracted with dichloromethane, washed with distilled water, dried over anhydrous Na_2SO_4 and evaporated using rotavapour to obtain a brown solid. The crude compound was passed through a short bed of silica gel column using hexane and chloroform mixture (95 : 5) as eluent to yield a white solid³³. Yield: 7.2 g (73%).

(4-Octyldecyl)-4H-dithieno[3,2-b:2',3'-d]pyrrole (**3a**): A solution of 3,3'-dibromo-2,2'-bithiophene (0.6 g, 1.85 mmol) in anhydrous toluene (20 ml) was added *t*-NaOBu (0.391 g, 3.7 mmol), $\text{Pd}_2(\text{dba})_3$ (67 mg, 0.074 mmol) and BINAP (92 mg, 0.148 mmol). The reaction mixture was purged in N_2 for 10 min and a solution of alkyl amine (3.7 mmol) in toluene was added via syringe. The mixture was allowed to reflux overnight and then cooled and added in water. The organic layer was separated and the aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over anhydrous Na_2SO_4 and evaporated using rotavapour. The crude product was purified by column chromatography using silica gel and hexane–ethylacetate mixture (95 : 5) to obtain white solid of **3a**.

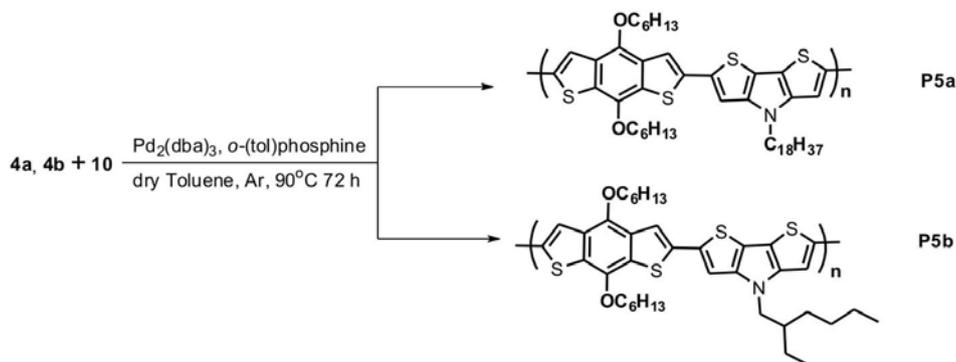
Yield: 82%. ^1H NMR (CDCl_3 , 400 MHz) δ : 7.15 (d, $J = 4.0$ Hz, 2H), 7.02 (d, $J = 4.0$ Hz, 2H), 4.21 (triplet, 2H), 1.88 (m, 2H), 1.27 (m, 30H), 0.90 (triplet, 3H).

^{13}C NMR (CDCl_3 , 100 MHz) δ : 14.27, 22.72, 27.02, 29.26, 29.39, 29.48, 29.58, 29.62, 29.72, 30.38, 31.95, 47.47, 110.96, 114.81, 122.77, 145.06. HRMS: $m/z = 432$.

(2,6-Dibromo-4-octadecyl-4H-dithieno[3,2-b:2',3'-d]pyrrole) (**4a**): To oven-dried 3-neck flask 0.431 g (1 mmol) of **3a** 4-octadecyl-4H-dithieno[3,2-b:2',3'-d]pyrrole and 50 ml of THF was added. The solution was cooled to -20°C and 0.373 g (2.2 mmol) *N*-bromosuccinimide was added in one portion. The solution was stirred for 24 h. Water was added to quench the reaction, followed by extraction with DCM the combined organic phases were washed with H_2O followed by brine. The organic phase was then dried with anhydrous Na_2SO_4 and the solvent was removed using rotavapour. The resulting solid was recrystallized from hexane/ethanol to give shiny, beige needles of **4a**.

Yield: 85%. ^1H NMR (CDCl_3 , 400 MHz) δ : 7.04 (s, 2H), 4.21 (triplet, 2H), 1.88 (m, 2H), 1.27 (m, 30H), 0.90 (triplet, 3H).

^{13}C NMR (CDCl_3 , 100 MHz) δ 141.50, 114.96, 114.26, 109.44, 47.57, 31.95, 30.25, 29.72, 29.61, 29.55, 29.43, 29.39, 29.18, 26.91, 22.71.



Scheme 2. Stille polymerization of monomers **4a** and **4b** with **10** to get copolymers **P5a** and **P5b**.

Polymerization by Stille cross-coupling reaction

A solution of equimolar amounts of the dibromo derivative (**4a**, **4b**) and the corresponding distannyl compound **10** (0.279 mmol) was taken in anhydrous toluene (20 ml) under Argon into a two-neck oven dried round-bottomed flask. To this solution, tris(dibenzylideneacetone)di palladium (0) (10 mg, 4 mol%) and tri(*o*-tolyl)phosphine (14 mg, 8 mol%) were added. The resulting solution was heated to reflux at 90°C for 72 h. After cooling to room temperature, the reaction mixture was added to 100 ml of MeOH and stirred for 2 h. The obtained polymers were filtered and Soxhlet extracted with methanol, acetone and hexane to remove the inorganic impurities and oligomers. Finally, the soluble fraction was collected by extracting with chloroform and evaporated to get the polymers **P5a** and **P5b** (Scheme 2).

P5a: ^1H NMR (400 MHz, CDCl_3) δ 7.43 (br, 1H), 7.08 (br, 1H), 6.88 (br, 2H), 4.27 (br, 6H), 1.96 (br, 8H), 1.26 (br, 42H), 1.08 (br, 8H), 0.88 (br, 9H).

GPC Data: $M_n = 10,394$, $M_w = 20,283$ and PDI = 1.95

P5b: ^1H NMR (400 MHz, CDCl_3) δ 7.39 (br, 1H), 7.08 (br, 1H), 6.86 (br, 2H), 4.26 (br, 6H), 1.96 (br, 6H), 1.74 (br, 6H), 1.43–1.26 (br, 27H), 1.08–0.88 (br, 12H).

GPC Data: $M_n = 10,011$, $M_w = 18,941$ and PDI = 1.89.

Results and discussions

Stille coupling has emerged as one of the easy approaches for C–C coupling reaction between stannanes and halides. Distannane derivative of BDT, prepared from the previous known procedures and coupled with the dibromo derivative of DTP with catalytic amount of Pd(0). Oxidative addition of dibromo DTP to Pd(0) gives an organometallic intermediate, this undergoes transmetallation with distannane BDT derivative to give another reactive intermediate having trimethyl stannic group and bromo atom unreacted. These species undergo recursive coupling

cycles to add alternatively BDT and DTP moieties to generate polymer with high molecular weight. The chemical structures of all monomers and polymers were confirmed by ^1H and ^{13}C NMR.

^1H NMR spectra of copolymers **P5a** and **P5b** are shown in Figure 3. Broad peak at 4.27 ppm corresponds to protons from (–N–CH₂–) of DTP unit and (–O–CH₂–) from BDT unit. Peaks in the 0.88–2.01 ppm range correspond to the protons of long alkyl chain attached both to DTP and BDT units of the copolymers. There are four chemically different aromatic protons in repeating units of both copolymers and peaks corresponding to them are centered around 7.26 ppm (solvent peak). The molecular weight of these copolymers was characterized by GPC by standard polystyrene beads and found that $M_n = 10,394$, $M_w = 20,283$ for **P5a** and $M_n = 10,011$, $M_w = 18,941$ for **P5b** with polydispersity (PDI) index of 1.9 for both the polymers.

The UV-visible spectra of copolymers were recorded both in solution and solid state. The absorption spectra exhibits a dual band feature with λ_{max} at 535 and 566 nm in solution and 550 and 585 nm in solid state respectively. Evident red shift of 20 nm from solution to thin film is mainly due to the strong intermolecular interactions in the solid state. It can be seen that increase in the intensity of peak at 566 nm in solution for **P5a** on moving to solid state (585 nm) may be due to effective packing. **P5a** having linear octyldecyl chain shows an efficient packing in solid state leading to an enhanced intensity; however red shift remained the same for both the compounds. **P5b** having branched 2-ethylhexyl shows a minimum packing in solid state. Another interesting feature that can be observed from Figure 4b is that polymers absorb in the solar spectrum with a bandwidth of 200 nm. This gives an implication that polymers are of low band gap and possibility exists to harvest maximum number of photons in solar spectrum.

As discussed in the introduction, upon shining sunlight there is an electron hole pair (exciton) generated in polymer (donor) and subsequently photoinduced electron transfer takes place from the LUMO of donor to LUMO

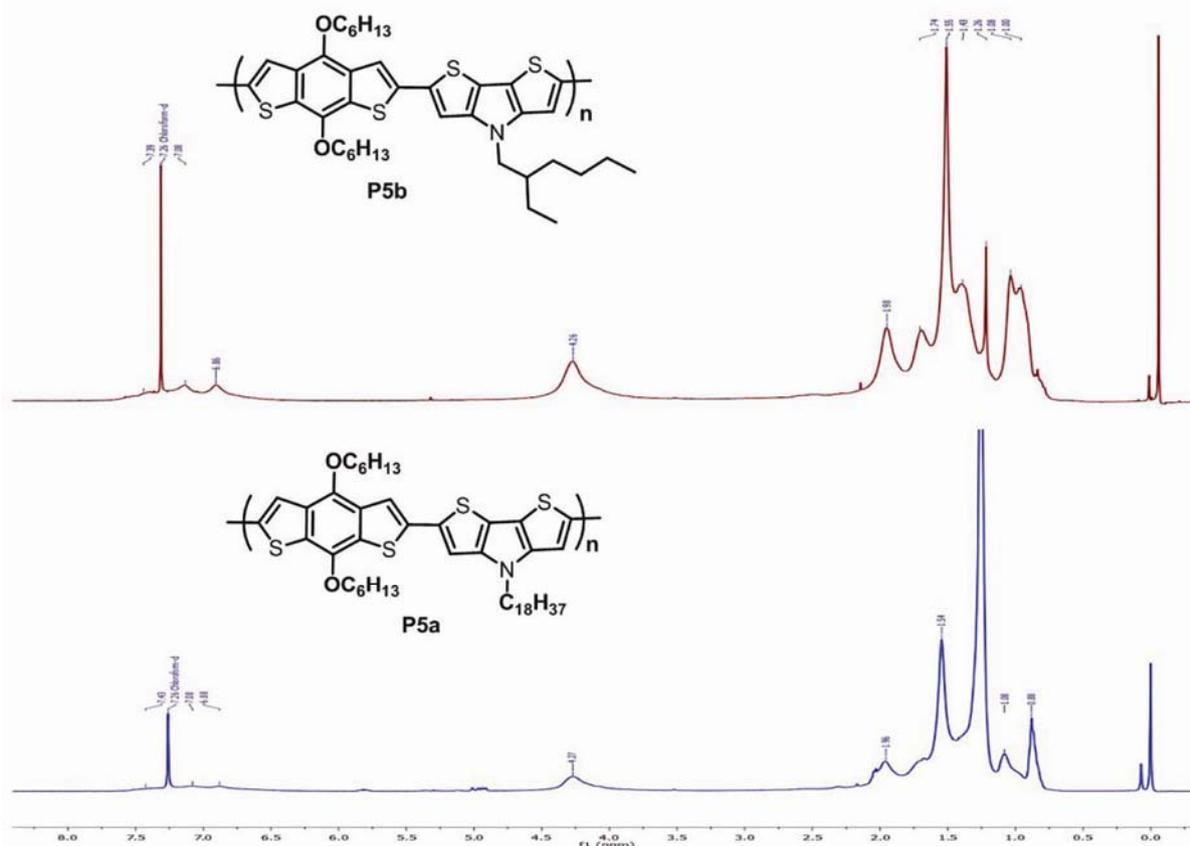


Figure 3. ^1H NMR of P5a and P5b in CDCl_3 .

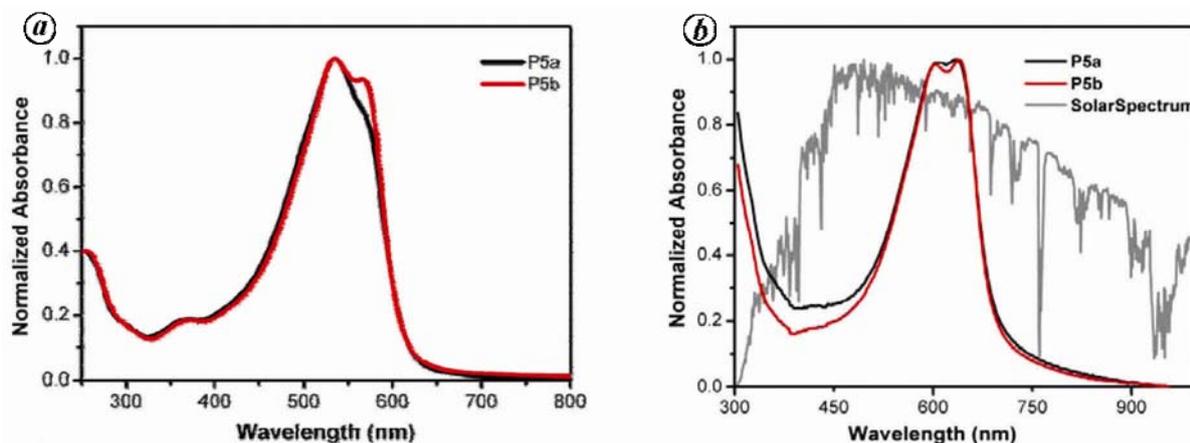


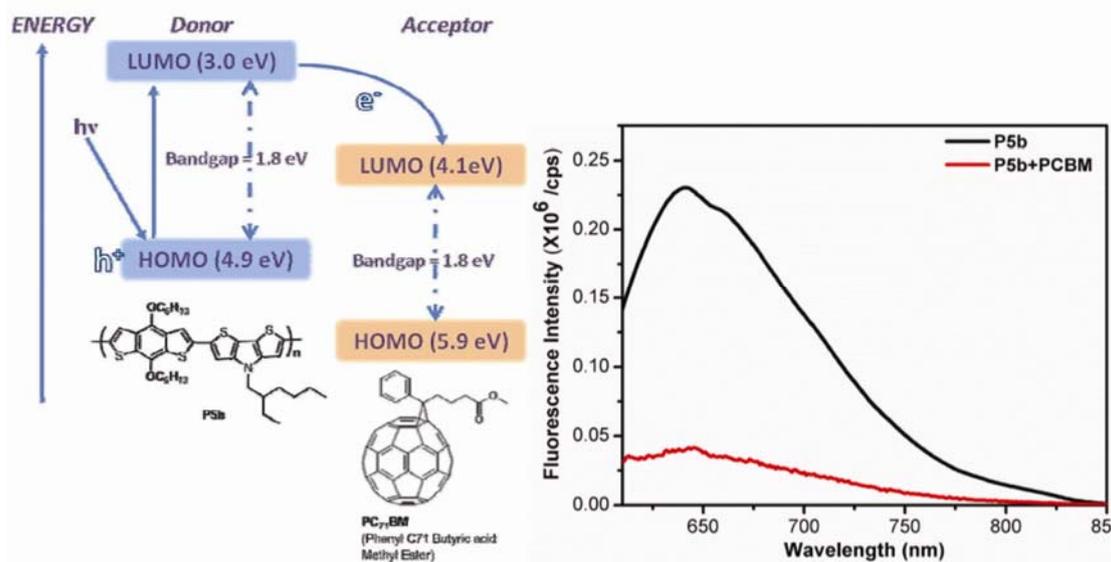
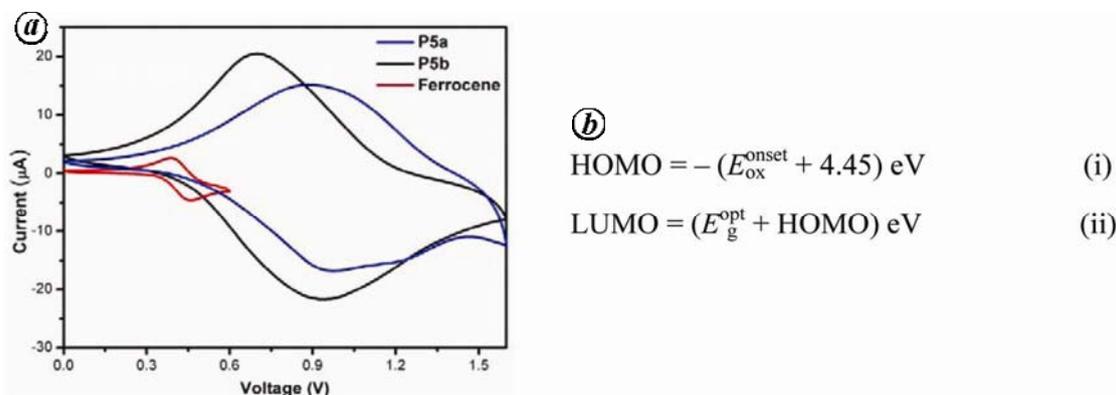
Figure 4. UV-vis spectra for copolymers P5a and P5b. *a*, Solution; *b*, Solid state in composition with solar spectrum.

of the acceptor. Figure 5 explains electron transfer process in BHJ of donor and acceptor which can be validated from the fluorescence quenching experiment. This charge transfer process is crucial for the performance of solar cells and can be followed by conducting steady-state fluorescence measurement of thin film of pure polymer and blend of polymer with acceptor. We have carried out

photoluminescence quenching measurements by preparing thin film of pure polymer and a blend (polymer and acceptor PCBM). The films were prepared by spin-coating on a glass substrate and fluorescence intensity of both the thin films was measured. The amount of reduction in fluorescence intensity in blend film would give an indication for the effective electron transfer process. It is

Table 1. Optical and electrochemical properties of **P5a** and **P5b**

Polymer	Solution		Thin film			CV		
	λ_{abs} (nm)	λ_{em} (nm)	λ_{abs} (nm)	λ_{em} (nm)	$E_{\text{g}}^{\text{opt}}$ (eV)	$E_{\text{ox}}^{\text{onset}}$ (V)	E_{HOMO} (eV)	E_{LUMO} (eV)
P5a	534	616	579	640	1.94	0.51	5.0	3.1
P5b	535	627	588	644	1.92	0.46	4.9	3.0

**Figure 5.** Energy level diagram indicating electron transfer process; spectrum for the fluorescence quenching of polymer **P5b**.**Figure 6.** *a*, CV for the polymer **P5a** and **P5b** along *b*, equation used for calculation of energy levels.

estimated from spectrum that fluorescence intensity is quenched by 94% by **P5b** polymer which suggests that these materials are suitable for the solar cell applications.

The electrochemical behaviour and oxidation/reduction properties of polymers are important parameters from device perspective and recorded from cyclic voltametry (CV) measurements. CV for both the molecules shows reversible oxidation peak and HOMO and LUMO levels were calculated from the plot (Figure 6) with reference to data obtained from Table 1.

Thin film morphology of **P5a** and **P5b** was studied by AFM and the corresponding 3D image is shown in Figure 7. Thin film of both polymers was smooth with some agglomerated particles. The rms roughness for **P5a** was 2.4 nm and 2.9 nm for **P5b**, which implies that the morphology of thin film was not influenced by the variation of alkyl chains.

The new family of conjugated polymers based on DTP is further under study for BHJ solar cells applications. These preliminary results suggest that, the family of

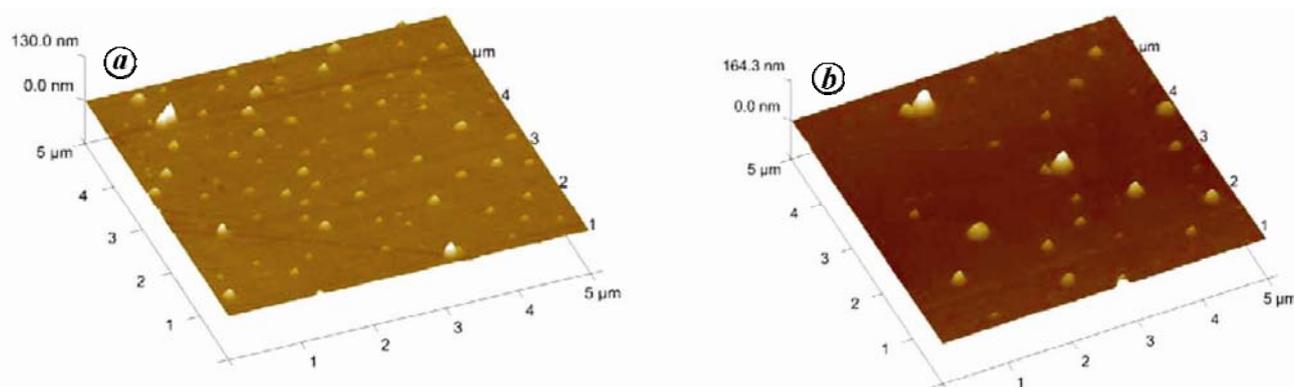


Figure 7. AFM of thin film of pure polymer (a) P5a and (b) P5b imaged under tapping mode.

DTP-based conjugated polymers are potential materials for optoelectronic devices.

Conclusions

Search for π -conjugated organic materials exhibiting high power conversion efficiency is the prime objective of ongoing OPV research in our group. We also synthesized two low-band gap materials having alternating DTP and BDT units with different alkyl chains using Stille coupling. Both the polymers were found to absorb in the solar spectrum and showed a great potential in terms of harvesting the solar energy. The UV-visible spectra of thin film showed a red shift of 20 nm in comparison to solution spectra with optical band gap around 1.93 eV. Electrochemical studies revealed that band gap of both the polymers to be around 2.0 eV. Fluorescence quenching of P5b showed quenching of 94%, indicating a good electron transfer process and due to low solubility of P5a quenching studies could not be performed. AFM showed smooth film morphology with rms roughness of 2.4 nm. It was evident that variation in the alkyl chain did not show any considerable change in the band gaps or morphology. These materials show the desired profiles for application into OPV device fabrication.

Declaration. Authors declare no conflicting financial interests.

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