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ARTICLE

Design of Medium Band gap Random Terpolymers Containing Fluorene Linked Diketopyrrolopyrrole and Thiophene Co-monomers: an Experimental and Theoretical Study

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B. SambathKumar, [ab‡] E. Varathan, [abc‡] V. Subramanian*[abc] and N. Somanathan*[ab]

In this study, we have designed new polymers **PTFDPP, PBTFDPP, PTTFDPP, PTCNEFDPP, PTDCNFDPP** and **PTPTFDPP** by employing D-A random copolymer strategy containing 9,9-dihexylfluorene (electron donor) linked to diketopyrrolopyrrole (electron acceptor) and thiophene comonomer (as donor as well as acceptor). Their optical band gap, HOMO and LUMO energy levels were estimated from ultraviolet-visible spectroscopy and cyclic voltammetry. By changing nature of thiophene from donor to acceptor state, their HOMO and LUMO energy levels and their optical band gap have been modified. It varies from 1.75 to 1.65 eV. A systematic density functional theory (DFT) calculations have been performed on model co-polymers to gain insights into the structural, electronic, and optical and charge transport properties. The experimental values are in close agreement with calculated electronic properties. Salient findings from both experimental and calculated values indicate that these new polymers can be efficiently exploited for the development of new donor materails for OPV applications.

Introduction

Revolution in bulk heterojunction solar cell (BHJ) started after the discovery of photoinduced charge transfer from conjugated polymer to fullerene in ultrafast time scale which enhances the photogeneration of charges to achieve high power effeciecny.[1] Today Bulk heterojunction solar cell based on conjugated polymer (electron donor) - fullerene (electron acceptor) system is considered as one of the promising renewable energy technologies.[2] The attractive advantage of BHJ is the low cost manufacturing of devices via solution processing technique.[3] Normally, BHJs have active layer consists of bicontinuous interpenetrating network between donor and acceptor for efficient dissociation of excitons at donor/acceptor interface.[4] It is well known that fullerene acts as a standard n-type acceptor due to its unique properties such as strong electron affinity, good electron mobility, favourable nanophase separation with polymer for efficient excitons dissociation and associated electron transfer in femtosecond scale from polymer.[5] However, synthesizing an ideal donor material is a challenging task because it should balance all other photovoltaic parameters like open circuit voltage (V_{oc}), short circuit current (J_{sc}) and fill factor (FF) which are directly proportional to power conversion efficiency, (PCE = (J_{sc}* V_{oc}* FF)/P_{in}), where P_{in} is the input light power.[6,7] Therefore, a conjugated polymer needs the following characteristics to behave as an ideal donor: (i) strong and broad absorption in visible and near IR-region in order to harvest more photon from the solar spectrum which increases $J_{sc,}$ (ii) optimized HOMO and LUMO energy levels which drive efficient dissociation of exciton at donor/acceptor interface that enhances $V_{oc.}$, and (iii) high charge carrier mobility and nanoscale phase separation for avoiding recombination and efficient exciton dissociation which helps in improving FF of the device. These requirements facilitate high open circuit voltage (V_{oc}), short circuit current density (J_{sc}) and fill factor (FF) leading to high power conversion efficiency.[8-10] Designing such ideal donor material can be carried out by inserting a push-pull (electron rich donor – electron poor acceptor (D-A)) chromophores in polymer chain. In such a system, intra-molecular charge transfer from donor to acceptor leads absorption towards longer wavelength direction, so that the absorption of the co-polymers is broadened and also in such a system HOMO of the polymer is mainly controlled by the donor unit and LUMO is modulated by the acceptor fragment.

[a] CSIR -Central Leather Research Institute, (CSIR)-CLRI,Adyar,Chennai-600020 ,India E-mail: nsomanathan@rediffmail.com; Fax: +91-44-24911589; Tel: +91-44-24437189; E–mail: subuchem@hotmail.com, subbu@clri.res.in. Tel.: +91 44 24411630. Fax: +91 44 24911589.Address here.
[b] CSIR-Network of Institutes for Solar Energy, India.
[c] Academy of Scientific and Innovative Research(AcSIR), Anusandhan Bahavan, 2 Rafi Marg,Newdelhi 110001,India
‡ These authors contributed equally to this work

† Electronic Supplementary Information (ESI) available: Detailed synthetic procedure for monomers and copolymers, ^{1}H, ^{13}C NMR, EI mass spectra (M4, M5 and M6) and FT-IR for monomers and copolymers and optimized geometries of the representative dimer conformations of Polymers

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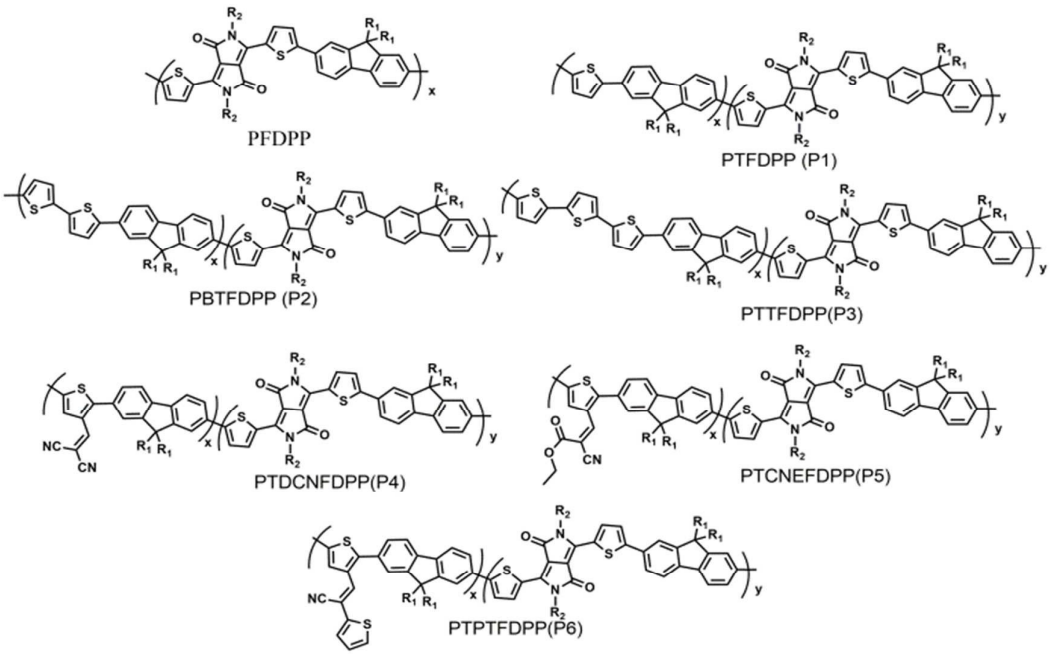

Figure 1. Structure of the DihexylFluorene linked alternating random copolymers PTFDPP (P1), PBTFDPP (P2), PTTFDPP (P3), PTDCNFDPP(P4), PTCNEFDPP(P5), and PTPTFDPP(P6), x:y=1:1,R_1=hexyl and R_2=octyl.

Previous studies revealed that by proper selection of the donor and acceptor unit in a polymer chain, it is easy to fine tune the FMO (HOMO and LUMO) energy levels.[11] Apart from alternate D-A copolymer, recently terpolymer strategy is found to be highly attractive approach for designing an ideal donor material. In this approach, a judicious selection of multiple chromophores in the polymer chain has been made that leads to two distinct absorption bands from two different donor or acceptor units which are in conjugation with another donor or acceptor unit.[12,13] Among various acceptor units, diketopyrrolopyrrole is a highly attractive molecule due to its well conjugated rigid structure, strong π-π interaction, electron withdrawing lactam group, and absorption in near-infrared region (NIR) which makes diketopyrrolopyrrole as a best electron acceptor.[14] One of the possible approaches of getting deep HOMO value is by inserting fluorene in the polymer chain that results in enhanced V_{oc} which is directly related to HOMO of the donor and LUMO of the acceptor. Andersson et al reported various fluorene copolymers with deep HOMO level and high open circuit voltage.[15] In this investigation, six different random conjugated copolymers using diketopyrrolopyrrole as an electron acceptor with variable thiophene comonomer as donor as well as acceptor have been designed and it was shown in Figure 1. Copolymerizing both these units with 9,9-dihexylfluorene using Suzuki coupling offers a new class of conjugated polymers. By systematically varying the thiophene segments (from donor nature to acceptor), the band gap, HOMO and LUMO energy levels can be fine-tuned. The structure-property relation was characterized using cyclic voltammetry, optical absorption and electronic structure calculations. In the literature, numerous quantum-chemical calculations on the co-polymer and small molecules systems have been performed on the donor-acceptor systems. These studies have provided valuable information on the design and development of ideal donor molecules/polymers for BHJs.[16] In this study, both experimental techniques and density functional theory (DFT) based calculations have been carried out on D-A random copolymers based on DPP, fluorene and thiophene building blocks using B3LYP/6-31G* level to gain insight into the structural, optical, electronic and charge transport properties of these new polymeric systems.

Experimental Section

Materials and Methods

2-Thiophenecarbonitrile, dimethyl succinate, potassium tert-butoxide, 2-methyl-2-butanol, 3- thiophenecarboxaldehyde, malononitrile, ethyl cyanoacetate, 2-thiopheneacetonitrile, 5,5'-dibromo-2,2'-bithiophene, 5,5''-dibromo-2,2':5',2''-terthiophene, 2,5-dibromothiophene, 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester, aliquate, piperidene, tetrtetrakis(triphenylphosphine)palladium(0), and N-bromosuccinimide (NBS) were purchased from Aldrich chemical company and used without any further purification. Vibrational spectra were carried out on ABB MB3000 FT-IR spectrophotometer. Mass spectra were collected using JEOL GC MATE II instrument. The ion source was operated in the electron ionization mode (EI:70 eV, 220°C).

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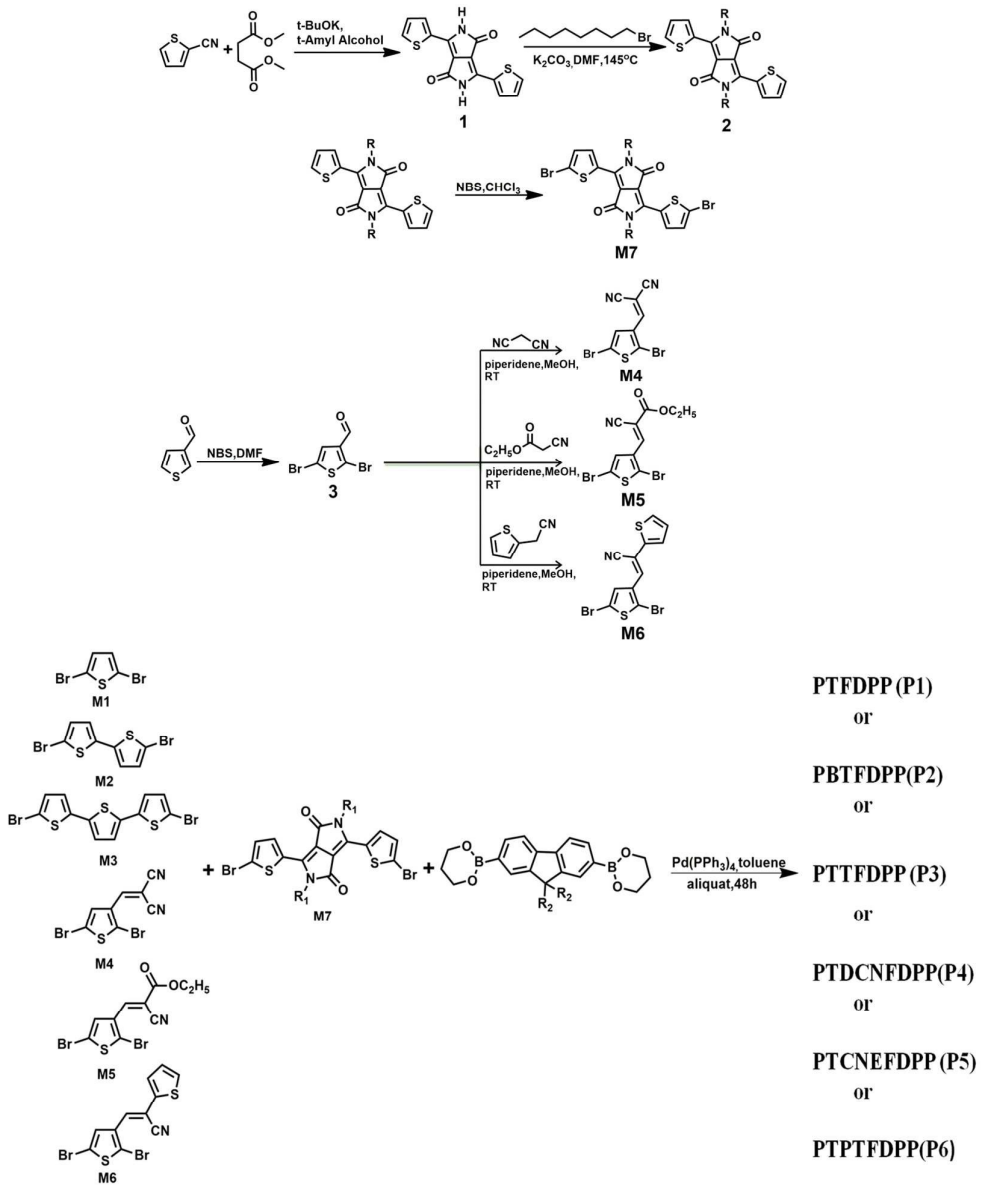

Scheme 1. Synthetic route for monomer (M4, M5, M6 & M7) and random polymers PTFDPP (P1), PBTFDPP (P2), PTTFDPP (P3), PTDCNFDPP (P4), PTCNEFDPP (P5) and PTPTFDPP (P6).

^{1}H and ^{13}C NMR spectra of compounds were recorded on Bruker 400 MHz NMR spectrometer. UV-Visible absorbance was carried out on Varian Carey 50 Bio UV-Visible spectrophotometer. Elemental analyses for monomers and polymers were carried out on Euro Vector S.P.A, Euro EA 3000 CHNS Elemental analyzer. Cyclic voltammetry measurements were carried out using CHI 600D electrochemical workstation with platinum disc electrode as working electrode, Ag/AgCl electrode as reference electrode and platinum wire electrode as counter electrode. Measurements in cyclic voltammetry were performed by coating a thin layer of polymers on platinum Disc electrode. The CV instrument was calibrated using ferrocene/ferrocenium ion (Fc/Fc^{+}) redox couple as external standard with potential of 0.09eV against (Ag/Ag+).

Computational Methodology

Density functional theory (DFT) has been extensively applied to predict the geometries and electronic properties of Donor-Acceptor systems comprising of oligomers and co-polymers.[17] Calculated structures and properties of organic electronic materials in the ground state (S_0) with B3LYP hybrid functional often provide close agreement with crystal geometries when compared to other density functionals.[18] Thus, All the structures in their ground state were optimized at the B3LYP/6-31G* level of theory.[19] The fully optimized structures were further characterized by harmonic vibrational frequency analysis to ensure that a real local minimum was found without imaginary vibrational frequencies. The solubilising alkyl groups from fluorene and DPP units were modelled as

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methyl group due to computation limitation. Using the gas phased optimized ground state geometries, the absorption spectral properties in chloroform ($CHCl_3$) were calculated by employing time dependant density functional theory (TD-DFT) method combined with Polarizable Continuum Model (PCM) at B3LYP/6-31G* level. The Swizard program was used to evaluate the singly excited state configurations to each electronic transition.[20] All the calculations were carried out using Gaussian 09 program package.[21]

Results and Discussion

Synthesis and Thermal stability

All the copolymer were synthesised using Suzuki polycondensation, using 1:1 feed ratio of appropriate dibromo comonomer with equivalent amount of 9,9-dihexylfluorene-2,7-diboronic acid bis(1,3-propanediol) ester in the presence of tetrakis(triphenylphosphine)palladium(0) as a catalyst, potassium carbonate as base in toluene/water mixture at 90 °C for 2 days and their synthetic routes were shown in scheme 1. The actual ratio in the terpolymer was determined by elemental analysis and it has good agreement with the molar feed ratio. The detailed procedure is described in the supporting information. All the copolymers exhibit good solubility in common organic solvents such as THF, chloroform, chlorobenzene and dichlorobenzene. Gel-permeation chromatography (GPC) was carried out to find weight-average molecular weight (Mw), number-average molecular weight (Mn), and polydispersity index (PDI) in tetrahydrofuran solution relative to polystyrene standard and the results are tabulated in Table 1. The thermal properties of the polymers were analysed using Thermogravimetric analysis (TGA). Results are summarized in Table 1 and presented in Figure 2. All the polymers showed good thermal stability up to 383−407 °C with 5% weight loss.

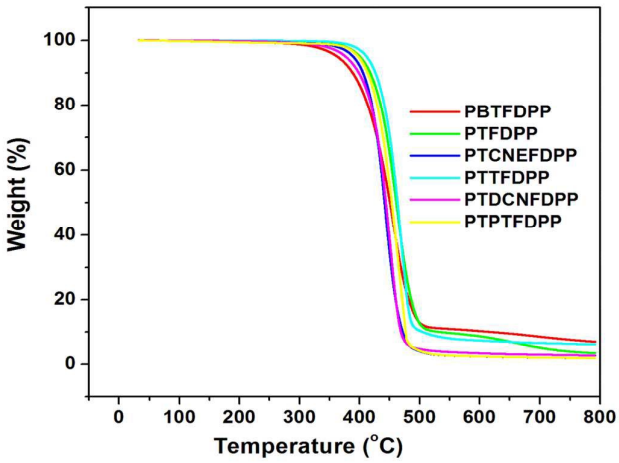

Figure 2. TGA plots of the copolymers with a heating rate of 10 °C min-1 in an inert atmosphere.

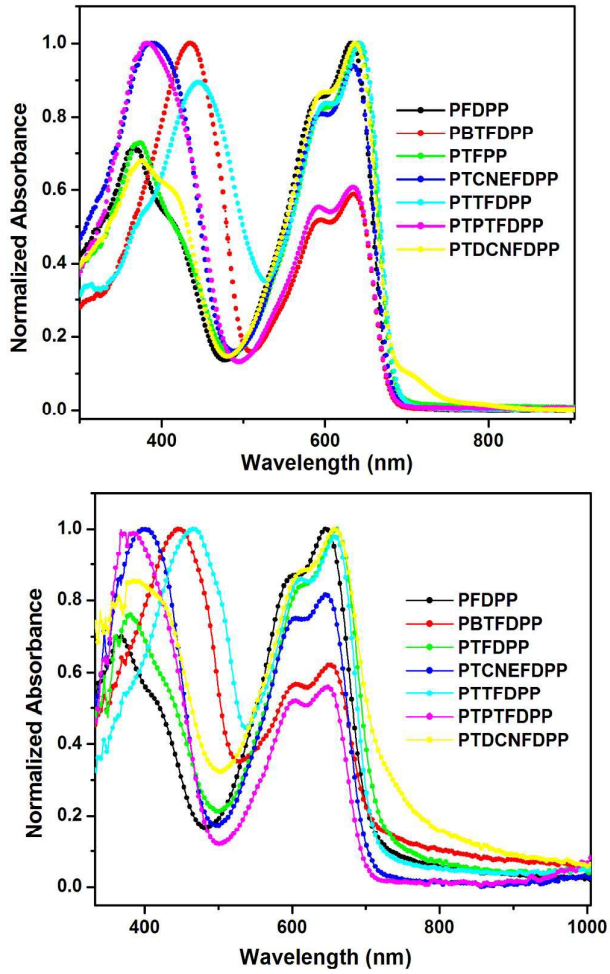

Figure 3. UV-vis absorption spectra of copolymers (a) in dilute chloroform solution and (b) in thin films.

Optical Properties

The UV-visible absorption spectra for all the copolymers in dilute chloroform solution and also in thin film are shown in Figure 3. The corresponding optical parameters are listed in Table 1. It is worth note that all the copolymers exhibit red shift in thin film when compared to solution which suggests the strong π-π intermolecular interaction in thin film. All the six copolymers exhibit three different absorption bands and the first band appears at 350-550 nm in short wavelength region. This band corresponds to localized π−π* transitions of the polymer backbone. The second and third bands are observed at 500−800 nm in long wavelength region which can be attributed to intramolecular charge transfer (ICT) from donor to acceptor. For polymer PTFDPP, PBTFDPP, and PTTFDPP, the increase in thiophene segment from 1 to 3 results in red shift as seen in short wavelength region from 380 to 466 nm due to enhancement in conjugation in the main chain.[22]

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In contrast to P1, P2 and P3 the absorption maxima for P4, P5 and P6 systems exhibit blue shift in both solution and thin film probably due to highly sterically hindered structure which affects the planarity of polymer backbone and reduction in the conjugation length. To gain more insights into the excited state properties of the polymers, TD-DFT calculations were performed. Calculated excited-state vertical transition energies, oscillator strengths, and transition electronic configurations are given in Table 2. It can be seen that experimental absorption peaks are well reproduced by the calculations. For all polymer systems, the $S_0 \rightarrow S_1$ transition is primarily a HOMO→LUMO transition (98-99%). All the co-polymers show three optical transitions, in the range of 362-406 nm arising from delocalized π-π* transition in the main chain and other two peaks occur in the range between 416-584 and 631-649 nm originating from a charge transfer state in the D-A segment. After examining the predominant component of the molecular orbitals involved in the pertinent transitions, one can see that lowest singlet $S_0 \rightarrow S_1$ excited state with high-oscillator strength (between 1.3926-2.0018), corresponds predominantly to a transition between the HOMO and the LUMO levels. Other single excitations that contribute to the total excited state wave function involve transitions between HOMO to HOMO-1 and HOMO-1 to LUMO and LUMO+1 level.

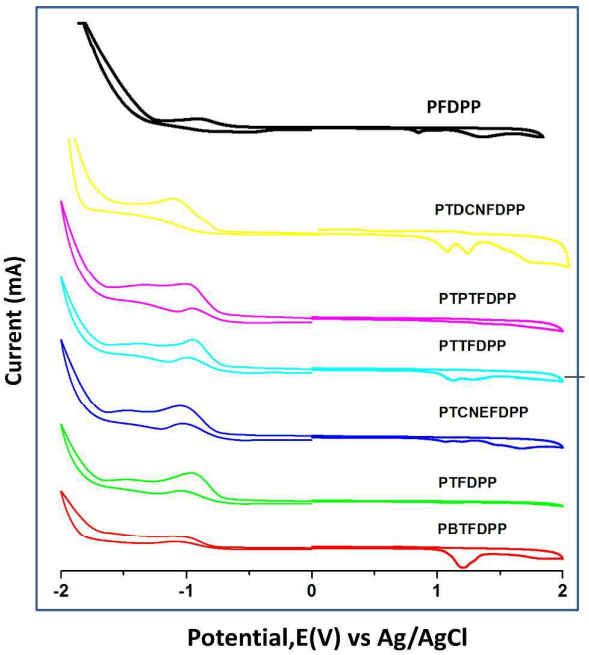

Figure 4. Cyclic voltammetry of copolymers thin film in 0.1m $TBAPF_6$ in acetonitrile solution.

Electrochemical Properties

In order to understand the electrochemical properties of copolymer cyclic voltammetry experiments were recorded in 0.1M

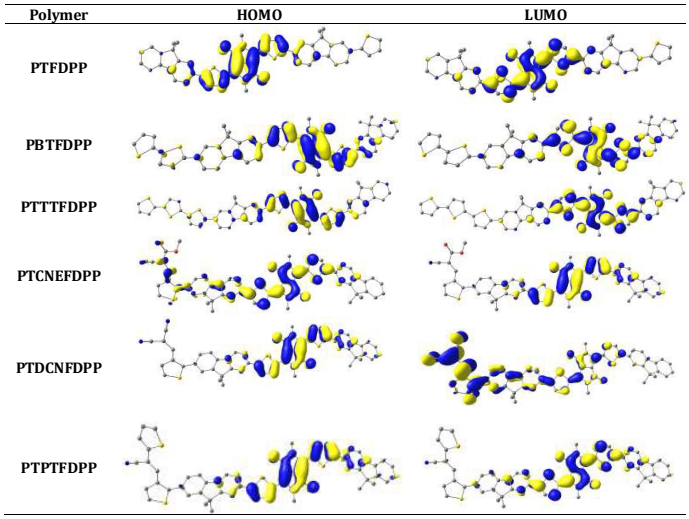

Figure 5. Pictorial representations of the frontier molecular orbitals for PTFDPP, PBTFDPP, PTTTFDPP, PTCNEFDPP, PDCNFDPP and PTPTFDPP.

tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) solution of acetonitrile as a supporting electrolyte. Their HOMO, LUMO energy levels, electrochemical band gap and oxidation, reduction cycle was displayed in Table 3 and Figure 4. The HOMO and LUMO energy levels and the electrochemical band gap (E_g^{ec}) of six copolymers were estimated from the first onset oxidation potential (E_{ox}) and the reduction potential (E_{red}) from the following equation.[23]

$$\text{HOMO} = -e(E_{ox} + 4.71) \quad (\text{eV})$$

$$\text{LUMO} = -e(E_{red} + 4.71) \quad (\text{eV})$$

$$E_g^{ec} = e(E_{ox} - E_{red}) \quad (\text{eV})$$

The HOMO energy level of polymer P1, P2, P3, P4, P5 and P6 were calculated to be -5.65, -5.63, -5.66, -5.55, 5.58 and 5.64 eV respectively. Compared to polymers P4 and P5, polymers P1, P2, P3 and P6 exhibit deep lying HOMO energy levels which clearly indicates that the HOMO level of these polymer is primarily determined by the strength of donating thiophene comonomer. Interestingly the HOMO energy level of P4 and P5 with electron withdrawing pendant cyano group are lower (~0.1 eV in HOMO) when compared to P1, P2, P3 and P4 counterparts. However, there is no significant variation in LUMO energy level for all the polymers which clearly indicates the predominant role of DPP in LUMO energy level. The optimized geometries of model systems are shown in Figure SI.19. The HOMO and LUMO energies and HOMO-LUMO energy gaps (Eg) are given in Table 3. The calculated values are in good agreements with the experimentally calculated values in this study. For all the polymers the HOMO values are found to be PTFDPP ~ PBTFDPP~ PTTFDPP > PTPTFDPP > PTCNEFDPP > PDCNFDPP, and the LUMO values are in the sequence PTFDPP > PBTFDPP > PTTFDPP > PTPTFDPP > PTCNEFDPP > PDCNFDPP. These results reveal electron withdrawing capability of the thiophene unit increases with substitutions. As a result di-cyano-substituted (PDCNFDPP) thiophene has lower HOMO-LUMO gap than others. It is clearly evident that the introduction of a stronger electron-withdrawing group onto the copolymer has a significant influence on reducing the HOMO and LUMO energy levels of

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Table 1. Optical and thermal Properties of Polymers P1-P6.

Polymer	λmax (nm) [a]Solution	[b]Thin film	λonset (nm) (thin film)	[c]Egopt (eV)	[d]T_d (°C)	[e]M_n (g/mol)	[f]M_w (g/mol)	[g]PDI
PFDPP	364,595,632	366,602,644	721	1.72	-	-	-	-
PTFDPP (P1)	374, 599, 640	379, 609, 659	725	1.71	389	9138	17841	1.95
PBTFDPP (P2)	435, 594, 635	446, 604, 651	709	1.75	383	10821	20791	1.92
PTTFDPP (P3)	443, 600, 643	464, 607, 659	717	1.73	407	8708	18268	2.09
PTDCNFDPP (P4)	375, 594, 637	386, 611, 651	751	1.65	376	8265	18451	2.23
PTCNEFDPP (P5)	389, 591, 635	400, 602, 645	742	1.67	388	7939	16738	2.11
PTPTFDPP (P6)	383, 591, 635	384, 601, 647	734	1.69	397	7282	14390	1.98

[a]Solution absorption in CHCl3. [b]Absorption in thin film on quartz. [c]Optical band gap estimated from the onset of UV curve measured in thin film. [d] 5%Weight loss temperature measured by TGA under N_2. [e] Number-average molecular weight. [f]Weight-average molecular weight. [g]M_w/M_n.

Table 2. Excited-state vertical transition energies (E_{vert}, eV), oscillator strengths (arbitrary units), and electronic Configuration of the first excited state as determined with TD-DFT at the B3LYP/6-31G* level of theory

Polymer	E_{vert} (eV)	Cal λ_{max} (nm)	f (au)	Configuration	Exp λ_{max} (nm)
PTFDPP	1.96	631.7	1.6790	H→L (99%)	640
	2.80	442.4	0.2467	H-2→L(68%), H→L+1(24%)	599
	3.34	370.3	0.4571	H-3→L(82%), H-1→L+1(9%)	374
PBTFDPP	1.94	637.7	1.8394	H→L(99%)	635
	2.74	452.1	0.1994	H→L+1(59%), H-2→L(31%)	594
	3.04	406.8	0.9349	H-3→L(67%), H-1→L+1(23%)	435
PTTFDPP	1.93	642.6	2.0018	H→L(98%)	643
	2.63	471.3	0.6049	H→L+1(86%)	600
	2.85	435.4	0.9129	H-1→L+1(56%), H-3→L(26%)	443
PTCNEFDPP	1.95	636.2	1.6396	H→L(99%)	634
	2.84	436.9	0.6819	H-2→L(85%),	592
	3.38	366.5	0.3301	H-1→L+1(7%) H-0→L+3(89%)	389
PTDCNFDPP	1.91	649.7	1.3926	H→L(98%)	637
	2.12	584.3	0.2937	H→L+1(99%)	594
	3.35	369.7	0.3512	H→L+3(90%)	375
PTPTFDPP	1.96	632.9	1.6797	H→L(99%)	635
	2.98	416.6	0.5990	H-1→L+1(54%),	591
	3.41	362.5	0.2249	H-3→L(35%) H→L+3(56%), H-2→L+1(25%)	383

the copolymer. The pictorial representations of the molecular orbital densities are given in Figure 5. For all the polymers (except PTCNEFDPP), the HOMO level lies on DPP and the contribution from the fluorene and thiophene are negligible. Therefore, there is a weak electron coupling between the donor (fluorene and thiophene) and acceptor. In the case of PTCNEFDPP, the bonding interaction between the donor and acceptor facilitates the strong electronic coupling between the subunits. Hence, the electron density of distribution of HOMO is delocalized over the DPP, fluorene and thiophene units. The electron densities of LUMO of all the polymers are localized on the DPP unit only, except for PTDCNFDPP. In PTDCNFDPP, the electron density of LUMO electron is delocalized between DPP, fluorene and substituted thiophene units. However, close analysis of these orbitals reveals that the LUMO is predominantly localized on the dicynao substituted thiophene. As a result, polymer PTDCNFDPP has a clear charge separation when compared to other polymers.

Hole Mobility of co-polymer

Previous studies revealed that the charge mobility of organic molecules can be well described by the incoherent hopping

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Table 3. Frontier Molecular Orbital Energies and HOMO-LUMO Energy Gaps (Eg) As Determined at the B3LYP/6-31G* Level of Theory and Electrochemical properties of polymer calculated using cyclic voltammetry measurement.

	Theory					Exp				
Polymer	HOMO (eV)	LUMO (eV)	E_g	IP	EA	E_{ox}^{onset} (V)	E_{red}^{onset} (V)	[a]HOMO (eV)	[a]LUMO (eV)	[b]E_g^{elc}
PFDPP	-	-	-	-	-	0.91	-0.73	-5.62	-3.98	1.64
PTFDPP (P1)	-4.73	-2.52	2.20	5.56	-1.64	0.94	-0.73	-5.65	-3.98	1.67
PBTFDPP(P2)	-4.73	-2.53	2.20	5.51	-1.68	0.92	-0.76	-5.63	-3.95	1.68
PTTFDPP(P3)	-4.73	-2.54	2.19	5.45	-1.73	0.95	-0.71	-5.66	-4.00	1.66
PTCNEFDPP	-4.86	-2.68	2.18	5.72	-1.93	0.87	-0.73	-5.58	-3.98	1.60
PTDCNFDPP	-4.87	-2.77	2.10	5.73	-2.03	0.84	-0.78	-5.55	-3.93	1.62
PTPTFDPP(P6)	-4.81	-2.61	2.20	5.64	-1.82	0.93	-0.70	-5.64	-4.01	1.63

[a] HOMO and LUMO were calculated using equations $E_{HOMO}/_{ELUMO}$=[Eonset+4.71)$_e$V. [b]E_g^{elc} band gaps of the polymers were calculated by the eqn E_g^{elc}=(E_{ox}^{onset} - E_{red}^{onset}).

model.[24] In this context, the charge transport is viewed as a charge exchange reaction.

$$M^{n} + M^{i} \rightarrow M^{i} + M^{n} \quad \ldots\ldots\ldots\ldots [1]$$

where, M^n represents the neutral state of the system and M^i represents the ionic state of the system. The hole/electron transfer rate can be expressed by the standard Marcus-Hush equation (2).[24]

$$K_{\text{hole/electron}} = \left(\frac{4\pi^2}{h}\right)\frac{1}{\sqrt{4\pi k_B T\,\lambda_{\text{hole/electron}}}}V^2\,\exp\left(-\frac{\lambda_{\text{hole/electron}}}{4k_B T}\right) \ldots [2]$$

Where T is the temperature, λ is the reorganization energy, V is the electronic coupling matrix element (transfer integral) between neighboring molecules in the organic single crystal, h is the Planck constant and k_B is the Boltzmann constant. It is evident from the equation 2 that there are two key parameters which determine the charge transfer rate, λ and V. Molecules having maximum transfer integral with minimum V_{ab} are expected to show optimal transport properties. The total reorganization energy of the molecule is given by the sum of internal and external reorganization energies. The former results from changes in the geometry of individual molecules and the latter, from changes in the polarization of the surrounding molecules upon going from the neutral to the charged state and vice versa. As the contribution from intermolecular polarization is expected to be very small in non-polar systems therefore the main contribution to the total reorganization energy would be from internal reorganization. In this study the internal reorganization energy (for hole and electron) is calculated by using the following equations (3) and (4).

$$\lambda_{+} = \lambda_1 + \lambda_2 \ldots\ldots\ldots\ldots [3]$$
$$\lambda_{-} = \lambda_3 + \lambda_4 \ldots\ldots\ldots\ldots [4]$$
$$\lambda_1 = E^{+}(M_0) - E^{+}(M^{+}); \quad \lambda_1 = E^{0}(M^{+}) - E^{0}(M_0)$$
$$\lambda_3 = E^{-}(M_0) - E^{-}(M^{+}); \quad \lambda_1 = E^{0}(M^{+}) - E^{0}(M_0)$$

Where E^0 (M_0), E^+ (M^+), and E^- (M^-) respectively denote the total energy of neutral, cationic, and anionic species at their optimized geometries. E^+ (M_0) and E^0 (M^+) denote the total energy of the cationic and neutral species at their optimized geometry of M_0 and M^+ respectively. Similarly, E^- (M_0) and E^0 (M^-) represent the total energy of the anionic and neutral species at the optimized geometry of M_0 and M^- respectively. The reorganization energies for electrons (λ_-) and holes (λ_+) of the molecules were computed at the B3LYP/6-31G* level. It has been evident from the previous studies that B3LYP functional with 6-31G* basis set provides most reliable results on the reorganization of organic molecules.[18]

The transfer integral V_{ab} represents the strength of electronic coupling between the two adjacent neighboring molecules a and b. V_{ab} can be calculated based on Koopmans' theorem[25] by assuming that the interacting molecules are identical, symmetrically equivalent and also have the same site energies. This method have been most frequently used in the literature for the estimation of transfer integrals in organic semiconductors.[18,24]

$$V_{ab} = \frac{E_{H/L+1} - E_{H-1/L}}{2} \quad \ldots\ldots\ldots\ldots [3]$$

Where EH/L+1 and EH-1/L are the energies of HOMO/LUMO+1 and HOMO-1/LUMO, respectively, obtained from the closed shell configuration of neutral state of two stacked molecules. Once the charge transfer rate is obtained by eqn. (2), the hopping mobility can be estimated by the Einstein relation, equation (6).

$$\mu_{\text{hop}} = \frac{eD}{k_B T} \quad \ldots\ldots\ldots\ldots [4]$$

Where T is temperature, kB is Boltzmann constant, and D is the diffusion coefficient. The relation between D and kct for a one dimensional system is given by D = l2kct, where l is the space distance between two interacting molecules. The calculated reorganization energy (λ_+) values are listed in Table 4. From the table we can see that, calculated λ_+ values for the **PTFDPP, PBTFDPP, PTTTFDPP, PTCNEFDPP, PDCNFDPP** and **PTPTFDPP** range from 0.20-0.28 eV, which are comparable to the reported values for donor materials for BHJ in the literature.[26] This finding suggests that these systems are donor materials for the BHJs. For the co-polymers, λ_+ values decrease in the following order: **PTCNEFDPP~ PDCNFDPP> PTFDPP> PTPTFDPP> PBTFDPP> PTTFDPP**. This shows that PTTFDPP has good charge transfer property when compared to all other co-polymers. Transfer integral (t), is another key parameter which

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Table 4. Calculated hole integral (th), reorganization energy (λ), hole-transfer rate (kh), and hole mobility (μh) of model co-polymer.

	λ_+	t_h	K_h (S^{-1})	μ ($cm^2V^{-1}s^{-1}$)
PTFDPP	0.27	0.12	3.36×10^{13}	1.84
PBTFDPP	0.24	0.07	1.62×10^{13}	0.93
PTTFDPP	0.20	0.05	1.34×10^{13}	0.90
PTCNEFDPP	0.28	0.05	5.20×10^{12}	0.28
PTDCNFDPP	0.28	0.01	2.08×10^{11}	0.02
PTPTFDPP	0.25	0.02	1.18×10^{12}	0.13

Table 5. The exciton binding energy (E_b) and the difference of electron affinities between acceptor (PCBM) and donor (co-polymers).

	PTFDPP	PBTFDPP	PTTFDPP	PTCNEFDPP	PDCNFDPP	PTPTFDPP
E_b (eV)	0.24	0.25	0.26	0.24	0.19	0.24
EA_A-EA_D (eV)[a]	1.78	1.77	1.76	1.62	1.53	1.69

$PCBM_{LUMO}$= 4.3 eV, [a]EA_A, EA_D are the electron affinities of the acceptor (PCBM) and donor (co-polymers).

is used to characterize transport behavior of the organic molecules. For organic molecules, intermolecular stacking is expected to be dominantly influenced by the π–π interactions. Hence, the initial geometry of the two monomers was co-facially stacked at the distance of ~3.5 Å, and then the structures were further optimized. The optimized structures of the dimers obtained at the M05-2X/6-31G* level of theory are presented in Figure SI 20. It is evident from the previous reports, accurate prediction of transfer integral for copolymer still is a challenge from the perspective of theory.[26] Hence, we have qualitatively used t_h and μ values for comparison. The charge transfer integrals for hole (t_h), charge transfer rates (K_h), and hopping mobilities (μ) were calculated respectively using equations 2, 3 and 4. The values are listed in Table 6. It can be noticed from Table 6, PTFDPP has the higher inter-molecular hole mobility of 1.84 $cm^2V^{-1}s^{-1}$ in comparison to all the co-polymers. The calculated hole mobility of the all the co-polymers varies from 0.02-1.84 $cm^2V^{-1}s^{-1}$, which is akin to those of previously reported values.[26] Hence, these molecules could be potential candidate for the donor molecules for the BHJs applications.

Exciton Binding Energy

It is evident from the previous study that exciton binding energy is another key parameter to determine the employability of these molecules in devices.[27] The exciton binding energy and efficiency of the cells are inversely correlated, implying that polymer with lower excitons binding energy produce electric current from the absorbed photons more efficiently. The inter-molecular interaction in amorphous organic materials is weak in contrast to inorganic counterpart. As a result, the exciton is Frenkel type in organic molecules.[27] Hence, in order to reduce the exciton binding energy, clear separation of HOMO and LUMO should be important. Efficient dissociation of excitons at the donor/acceptor interface is enhanced by proper alignment of the energy levels between the donor and acceptor layers in solar cells.[28] The condition for the efficient exciton dissociation to be energetically favourable is E_b, D < E_{AA}-E_{AD}. The EA_A and EA_D are the electron affinities of the acceptor (PCBM) and donor (co-polymers), which are approximated to the negative LUMO of the acceptor and donor. Here, E_b can be taken as the difference between the electronic and optical band gap energies. The electronic band gap is approximated as the energy difference between the HOMO and LUMO, while the optical gap is taken as the lowest excitation energy obtained from the TD-DFT calculation. The calculated exciton binding energy (E_b) and the difference of electron affinities between the acceptor and donor are listed in Table 5. It can be seen from the Table 5; all copolymers have small E_b of about 0.2 eV, which is less than corresponding difference between the electron affinities of the acceptor and donor. Hence, all copolymers may have efficient dissociation of excitons at the donor/acceptor interface and the above discussion is based PCBM as an acceptor.

Conclusion

In summary, six different copolymers based on fluorene (as donor), DPP (as acceptor) and different thiophene comonomer as donors as well as acceptors have been synthesised. The importance of changing thiophene fragments has also been systematically investigated. It is evident that the substitution of thiophene by suitable group significantly alters the electrochemical band gap. The electronic structure calculations on these model systems reinforce the same

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findings. All the copolymer exhibit good thermal behavior between 383 to 407 °C, which ensures the tolerance of thermal stress during device fabrication. A detailed DFT and TD-DFT study have been applied to characterize the structure and electronic properties of the model systems. Based on the Marcus electron transfer theory, the hole transfer rate and hole mobility of the molecules have been obtained. Overall experimental and DFT results indicate that these molecules can be used for the design and development of donor materials for OPV applications.

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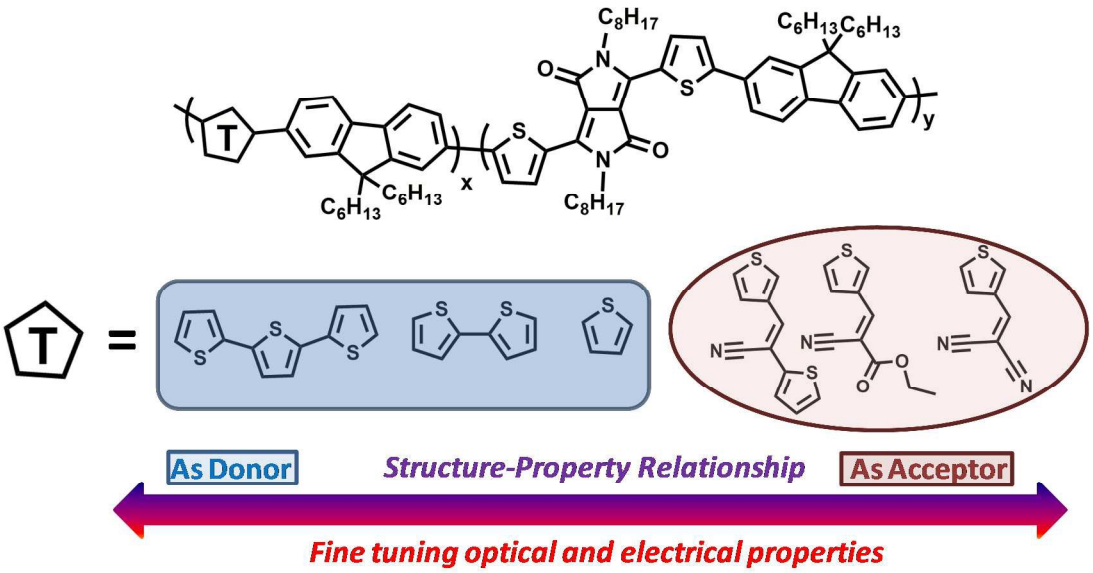
Table of Content

Design of Medium Band gap Random Terpolymers Containing Fluorene Linked Diketopyrrolopyrrole and Thiophene Co-monomers: an Experimental and Theoretical Study

B. Sambath Kumar,[ab] E. Varathan,[abc] V. Subramanian *[abc] and N. Somanathan *[ab]

Six different random Terpolymers were synthesised and their optoelectronic properties were fine-tuned by varying the thiophene strength.



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