Rational Design of Donor-Acceptor Based Semiconducting Copolymers with High Dielectric Constant

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Abstract:

An efficient photogeneration of free charge carriers has long been recognized as the paramount challenge in organic photovoltaic (OPV) devices. The low dielectric constant organic semiconductors fall short to reduce strong Coulombic interaction of tightly bound exciton and hence lead to a loss mechanism in OPVs due to charge-carrier recombination. To circumvent this problem, we adopt a strategy to enhance the dielectric constant of organic semiconductors by incorporating tetraethyleneglycol (TEG) side-chains. We report synthesis of three new semiconducting copolymers by combining thiophene substituted diketopyrrolopyrrole (TDPP) monomer with three other monomeric units with varying electron donating strength: benzodithiophene (BBT-3TEG-TDPP), TDPP (TDPP-3TEG-TDPP) and naphthalene diimide (PNDITEG-TDPP). BBT-3TEG-TDPP and PNDITEG-TDPP showed highest dielectric constants (~ 5) at 1MHz frequency suggesting efficient contribution of dipolar polarization from TEG side-chains. To understand the electronic contribution of the polymer backbone and the polarity of TEG side-chains, and the resulting enhancement of the dielectric constant, we further performed first-principles density functional theory calculations. Single-component organic solar cells (OSC) fabricated utilizing these polymers resulted in poor performance which is attributed to the absence of free charge generation. Furthermore, transient absorption spectroscopy studies show low exciton diffusion length as observed in donor-acceptor type conjugated polymers. Our results suggest that, the strategy of enhancing dielectric constant with polar side-chains is not sufficient to reduce Coulombic interaction between hole and electron in OSCs.
**Introduction:**

In contrast to inorganic semiconductors, optical excitation of an organic semiconductor leads to the formation of localized Frenkel exciton with significantly large binding energy than room temperature thermal energy ($k_B T$). As a result, the photogenerated charge carriers sustain a strong Coulombic interaction, which leads to significant geminate recombination losses in organic solar cells (OSCs).\(^1\)\(^-\)\(^2\) In OSCs, a second component with high electron affinity such as fullerene is incorporated into the active layer to surpass the exciton binding energy and establish bulk heterojunction (BHJ) between donor and acceptor.\(^3\)\(^,\)\(^4\) Although, the concept of BHJ has been continuously evolved and witnessed a record power conversion efficiency (PCE) of ~ 18% for single junction solar cells, the main disadvantage of BHJ is the morphology domains of donor and acceptor dictates the PCE of device.\(^5\)\(^,\)\(^6\) The morphology of donor/acceptor blend is very sensitive to the numerous parameters such as molecular structure of donor and acceptor, processing solvent, annealing temperature of thin film, spin-coating conditions and solvent additives.\(^7\)\(^,\)\(^8\) To explore the full potential of any newly synthesized polymer donor materials or small molecule acceptor, this ponderous process needs to be optimized.\(^9\)\(^,\)\(^10\) Despite these tedious efforts, phase separation of donor and acceptor domains is not limited to exciton diffusion length due to inherent thermodynamic instability of the blend.\(^11\)\(^,\)\(^12\) The difference in tendency of crystallization of donor and acceptor drive them to form microscopic domains larger than exciton diffusion length.\(^13\)\(^-\)\(^15\) These microscopic domains evolve further with the time and leads to spinodal decomposition of blend, resulting in shorter lifetime of OSCs.\(^8\)\(^,\)\(^12\)\(^,\)\(^15\)

Furthermore, the stringent energy criteria to accomplish efficient exciton dissociation through electron/hole transfer at the donor/acceptor interface leads to loss in energy. For instance, it was suggested that, the offset larger than 0.3 eV is imperative between the lowest unoccupied molecular orbital (LUMO) of acceptor with highest occupied molecular orbital (HOMO) level of donor, and thus leads to major loss in open-circuit voltage ($V_{OC}$).\(^16\) However, recent studies based on non-fullerene acceptor (NFA) based organic solar cells (OSC) have shown that excitons can be decoupled with a negligible energy offsets as low as 0.05–0.2 eV, and thus, small $V_{OC}$ loss is achieved.\(^17\)\(^,\)\(^18\) For example, NFA based OSCs comprising P3TEA as donor and a small molecule, SF-PDI\(_2\) as non-fullerene acceptor with a PCE of 9.5% exhibited only 0.05 eV energy offset and 0.61 eV energy loss.\(^17\) This has led to remarkable improvement in overall PCE of OSCs, albeit, still lower than the Shockley-Queisser
The low dielectric constant ($\varepsilon_r$) of organic semiconductor is pivotal to incur losses due to geminate and non-geminate recombination. For instance, single exciton recombination due to tightly bound charge carriers account for nearly 12% loss, whereas charge-transfer recombination accounts for more than 32% efficiency loss. This suggests that increasing dielectric constant of organic semiconductors can help surpass the Coulomb capture radius, resulting in an expected decrease in charge carrier recombination events (Figure 1a and 1b). To circumvent these problems, it is overwhelmingly important to increase the dielectric constant of organic semiconductors. Increasing dielectric constant can help surpass Coulombic interactions and effectively decrease radiative recombination. In addition, this would make the complicated BHJ device architecture no longer necessary, since the photon absorption leads to the creation of free charge carriers.

Towards this goal, only few attempts have been made from a synthesis perspective to and hence the progress in this regard has been very slow. In fact, the $\varepsilon_r$ of donor and acceptor systems utilized in high efficiency OSCs, are the least explored parameters. Functionally tuning organic molecules to achieve high $\varepsilon_r$, without compromising the solubility, bandgap, ionization potential, electron affinity and carrier mobilities is synthetically challenging.

The cautious approach in the scientific community to improve the $\varepsilon_r$ has largely focused on side-chain engineering which has negligible or minimal impact on electronic structure but significantly influences solid-state packing and energetic disorder. In one of the very first reports, triethylene glycol (TEG) side chains were introduced by Breselge et al. in a poly ($\rho$-phenylene vinylene) (PPV) derivative and an enhancement of $\varepsilon_r$ was reported. When blended with a fullerene derivative in BHJ, charge dissociation in the polymer was enhanced as compared to a less polar PPV derivative. But the above modified polar PPV moiety delivered poorer performance as compared to the less polar one when blended with fullerene derivative, which was attributed to the unfavourable morphology. In another report, when polar cyano groups were introduced to the end of butyl or octyl side chains of poly(dithienosilole-thienopyrroloiodione), improved $\varepsilon_r$ was observed. However, introduction of nitrile (-CN) groups increased the energetic disorder to the charge transport of the polymers and hence the hole mobility decreased but the electron mobility was enhanced, and the imbalance in charge transport led to inferior photovoltaic performances as compared
to their unsubstituted counterparts. In another contrasting and rather encouraging report, the introduction of nitrile groups, in terminal position of alkyl side chains of the electron deficient diketopyrrolopyrrole (DPP) unit of an indacenodithiophene (IDT)-based copolymer, improved the $\varepsilon_r$ as compared to the copolymer with alkyl side chain. The increment in $\varepsilon_r$ reflected in lower exciton binding energy and suppressed non-geminate recombination loss which collectively resulted in improved photovoltaic performance. These results showed that increased $\varepsilon_r$ of photoactive materials in MHz frequency range can definitely suppress the non-geminate recombination.

**Figure 1.** (a) Red-dotted line represents highly delocalized Wannier exciton in a two-dimensional crystal lattice of a typical inorganic semiconductor (b) The dotted red line represents Frenkel excitons, typically found in organic materials, which are localized at their site of creation unlike the Wannier excitons. (c) The schematic shows the backbone and sidechain dipolar polarization which enables to achieve high dielectric constant in case for organic semiconducting polymers.

To realize non-excitonic OSCs, high dielectric constant of organic materials not only desirable in low-frequency (MHz) but also at the high-frequency (THz) limit. However, increasing $\varepsilon_r$ via side-chain engineering vanishes in high frequency limits ($\sim$ THz) corroborating the fact that the enhancement of $\varepsilon_r$ is not electronic but only because of nuclear relaxations. The strategy of introduction of OEG based polar side chains have been shown to enhance the $\varepsilon_r$ of various DPP, PPV and fullerene derivatives to more than 5 in MHz region without compromising their carrier mobilities and solubility and has laid the foundation of realizing
single-component OSCs. Over the years, many such attempts have been made by various researchers by utilizing double cable polymers where donor and acceptor groups are covalently linked to each other. PCEs ranging from 0.1–5.5% have been achieved with many different double cable polymers and show lots of promise to simplify the device fabrication process. This has encouraged the community to develop more such molecules to envisage and understand the role of high \( \varepsilon_r \) in these solution-processable non-excitonic OSCs. Herein, we report synthesis of three new DPP-based donor-acceptor-donor type \( \pi \)-conjugated copolymers with DPP, benzodithiophene (BDT) and naphthalene diimide (NDI) groups. The properties of these three were compared with 2DPP-OD-TEG, a DPP based copolymer which was reported by our group earlier. Furthermore, we probe the role of backbone and side-chains on the improved \( \varepsilon_r \) using theoretical calculations. Two of these polymers show \( \varepsilon_r \sim 5 \) in MHz frequency range which is attributed to the contribution from dipolar polarization of the conjugated backbone. We further introduced multiple TEG chains with conjugated spacer units in side chains of two of the polymers to understand the effect of C-O bond polarization on \( \varepsilon_r \) (Figure 1c) BBT-3TEG-TDPP and TDPP-3TEG-TDPP have different backbones but same side-chains, yet BBT-3TEG-TDPP exhibits \( \varepsilon_r \) value almost twice as that of TDPP-3TEG-TDPP. Furthermore, we probed the generation, migration and decay dynamics of excitons in these polymers using femtosecond pump-probe spectroscopy. Surprisingly, we did not observe free charge carrier generation in any of these polymers. Although we have observed improved \( \varepsilon_r \) in MHz frequency range, the exciton dissociation occurs in short time (\( \sim \)ns) scale. The exciton diffusion length and lifetime were found to be highest for BBT-3TEG-TDPP which corroborates well with its highest dielectric constant among the four. Lowest structural disorder as evident from the Urbach energy (\( \varepsilon_U \)) extracted from photothermal deflection spectroscopy (PDS) agree well with BBT-3TEG-TDPP having high mobility and highest photovoltage in organic photovoltaics (OPV). Our complementary theoretical studies show that the contribution of dipolar polarization in the polymeric backbone along with the strength of donors/acceptors play an important role in achieving higher \( \varepsilon_r \) and hence can be utilized in future design principles to synthesize polymers with high \( \varepsilon_r \). The pertaining question of achieving free charge generation by improving the \( \varepsilon_r \) still remains open and is a matter of further investigation.
Results and Discussion:

The polymers were synthesized via Stille and Suzuki coupling reactions. The synthetic routes for the polymers BBT-3TEG-TDPP, TDPP-3TEG-TDPP and PNDITEG-TDPP are shown in Scheme 1. The required four monomers 3TEGTDPP-Br$_2$, BBT (SnBu$_3$)$_2$, TDPP (BE)$_2$ and NDITEG-Br$_2$ were synthesized according to literature procedures.$^{41,42}$ The polymer BBT-3TEG-TDPP was obtained with Stille coupling of BBT (SnBu$_3$)$_2$ and TDPP-3TEG-TDPP using Pd(PPh$_3$)$_4$ as a catalyst, whereas polymers TDPP-3TEG-TDPP and PNDITEG-TDPP were synthesized via Suzuki coupling reaction, using Pd$_2$(dba)$_3$ as the catalyst. The detailed procedures for the synthesis of polymers are described in the ESI. All the four precursors were purified by silica gel chromatography; structures and purity were verified by $^1$H NMR and $^{13}$C NMR. The final polymers were purified by Soxhlet extraction and characterized with GPC. The molecular weights of the polymers are determined using GPC and are tabulated in Table S1. All the polymers have poly dispersity indices (PDI) between 2-4. The molecular design is focused on coupling DPP with DPP substituted with alkyl or TEG side-chains (2DPP-OD-TEG and TDPP-3TEG-TDPP). We also coupled DPP with BDT (BBT-3TEG-TDPP) and NDI (PNDITEG-TDPP) units with different side-chains. To understand the effect of multiple TEG chains on optical and dielectric properties, without hindering molecular packing, a phenyl group substituted with three TEG chains was incorporated in DPP moiety with a triazole spacer. TDPP-3TEG-TDPP and 2DPP-OD-TEG have similar molecular backbone of TDPP-TDPP but with different side-chains, whereas, TDPP-3TEG-TDPP and BBT-3TEG-TDPP have similar side-chains but BBT-3TEG-TDPP has varied strength of D-A conjugated backbone. In addition, copolymer PNDITEG-TDPP was synthesized with a polar side-chains having ester functionality attached to the nitrogen of NDI group. The polymers substituted with polar side-chains found to be highly soluble in solvents like chloroform, chlorobenzene and TCE. Presence of unsymmetrical side-chains in TDPP-3TEG-TDPP and BBT-3TEG-TDPP enhanced their solubility as compared to 2DPP-OD-TEG.
Scheme 1. Synthesis of polymers with Suzuki and Stille coupling reactions.

Optoelectronic Properties:

The molecular structures of the copolymers are shown in Figure 2a. Figure 2b and 2c illustrate the optical absorption spectra of the polymers collected in solution and thin film. In solution, we observed a typical feature of donor-acceptor copolymers. The intramolecular charge-transfer (ICT) peak dominates at lower energy with high oscillator strength. In addition, multiple peak with low oscillator strength were observed below 500 nm, which are attributed to π-π* transition. The nature of the absorption spectra appeared similar for TDPP-3TEG-TDPP and 2DPP-OD-TEG whereas an apparent blue shift was observed for BBT-3TEG-TDPP and PNDITEG-TDPP. The extent of blue shift and oscillator strength was found to be
dependent on the nature of polymer molecular structure. This implies that the intramolecular electronic coupling within the polymer structure is strongly influenced by the strength of donor and acceptor. In thin films, red shifts were clearly observed for ICT and π-π* transition peaks, suggesting the enhancement of π–π stacking and planarization of polymer chains in the solid state. The apparent red shift in absorption and the change in vibronic peak ratio are the characteristics of polymer aggregates and highlights the importance of internal electronic structure. In this work, we have not investigated in detail the role of coherent coupling mechanism with the theoretical framework put forward by Spano et al.43,44

![Figure 2](image.png)

**Figure 2.** (a) Molecular structures of the synthesized co-polymers; UV-vis absorption spectra of polymers in (b) solution phase and in (c) thin film showing extended absorption till 1100 nm because of solid state intermolecular interactions, 2DPP-OD-TEG has lowest optical band gap among the lot.

To determine the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO) of the polymers, cyclic voltammetry (CV) was performed. Ferrocene was used as standard and the $E_{\text{HOMO}}$ was calculated using the formula $E_{\text{HOMO}} = 4.8$ eV + ΔE, where, ΔE is calculated by measuring the difference between the onset of oxidation and the half-wave potential of the ferrocene standard. Similarly, $E_{\text{LUMO}} = 4.8$ eV − ΔE, where,
ΔE is calculated by measuring the difference between the onset of reduction and the half-wave potential of the ferrocene standard. The cyclic voltammograms of all the polymers along with that of ferrocene standard are shown in Figure S4 (a-d). BBT-3TEG-TDPP shows three-step oxidation and reduction, PNDITEG-TDPP shows three-step reduction but only one-step oxidation which could be because of its highly electron-deficient core. 2DPP-OD-TEG shows one-step oxidation and reduction reversibly. TDPP-3TEG-TDPP exhibits two-step reduction but only single-step oxidation which could be due to electron-deficient DPP moieties stabilizing the negative polaron effectively compared to the hole. All the polymers show reversibility in reduction half emphasizing on the fact that the negative polaron can be effectively stabilized in the core. Figure S4e shows the HOMO/LUMO levels of all the polymers. All being medium to low band gap polymers with deep lying LUMO levels and wide absorption show that these can potentially be applied in organic photovoltaics (OPV). The optical and electrochemical bandgaps of the polymers along with their HOMO/LUMO levels as extracted from CV are shown in Table 1.

Impedance Spectroscopy, Theoretical Studies and Single-component Organic Solar Cells:

The dielectric constants of all the polymers were accurately measured using impedance spectroscopy following the protocols laid by Hughes et al. The detailed method of sample preparation and measurement is given in supporting information. Precise care was taken not to overestimate the ε_r of the polymers. Table 1 summarises the ε_r values of all the polymers at 1 MHz measured at room temperature in absence of light. BBT-3TEG-TDPP shows highest ε_r among all followed by PNDITEG-TDPP. 2DPP-OD-TEG shows similar ε_r values as reported in literature before. TDPP-3TEG-TDPP shows the lowest value among the series which can be attributed to its minimal backbone polarization and low dipolar contribution from distantly positioned TEG groups from the backbone. The ε_r values of the polymers remained almost constant throughout the sweeping frequency range till 1 MHz (Figure 3(a-d)). The role of TEG chain in providing high dipolar polarization because of its tendency to reorient even in higher frequencies is well established. The values of ε_r are marginally lower in dark as compared to that in ambient light which is expected from these low band-gap semiconducting polymers (Figure 3a, 3b). The devices were reversely biased using DC to completely deplete the active layer of any charge carriers (Figure 3c, 3d), which was confirmed from the capacitance response converging into the geometrical value (C_g = ε_0ε_r/d)
(Figure S5, SI). Frequency independent capacitance values were observed for all the polymers signifying the depletion of all charge carriers from the device. The drop in dielectric constant values for all the polymers under DC bias was significant barring PNDITEG-TDPP which shows minimal drop. The role of side-chain could be playing a very crucial role here as it is different from the ones in the other three polymers.

Figure 3. Relative dielectric constants of four polymers measured using impedance spectroscopy in (a) stray light; (b) dark; under DC bias of (c) -0.5 V and (d) -1.0 V. The measurements were performed at RT with an AC drive voltage of 0.5 V.

The contribution of dipolar polarizations towards dielectric constant is evident from the Figure 3. Computational studies were conducted to understand the dipolar contribution of side-chains and backbone to dielectric constant in the case of the polymers reported in this study. In addition to the polymers at hand, we also studied model systems where the large side-chains are replaced by methyl or isopropyl substituents to separate out and understand the effect of the backbone. The calculated dipole moments of these molecules and their dimers are listed in Table 2. Please see the ESI for the optimized geometries of the original and model systems. Though many conformations are possible, in fact computationally
prohibitively large in the case of the actual systems with many substituents, we limit ourselves to one particular conformation where the thiol rings are in the anti-arrangement. The DFT calculations were carried out at B3LYP/6-31g(d) level of theory using G16 program.46–48

Table 1. Dielectric constant, optical and electrochemical bandgaps of polymers as determined using impedance spectroscopy, UV-visible spectroscopy and cyclic voltammetry, respectively. adielectric constant at 0.1 MHz in dark, bextracted from the absorption onsets of polymer thin films, cextracted from CV.

| Polymers            | $\varepsilon_r^a$ | Optical bandgap$^b$ (eV) | Electrochemical bandgap$^c$ (eV) | HOMO$^c$ (eV) | LUMO$^c$ (eV) |
|---------------------|------------------|--------------------------|---------------------------------|--------------|--------------|
| BBT-3TEG-TDPP       | 5.16 (5.09 ± 0.04) | 1.46                     | 1.59                            | -5.20        | -3.61        |
| PNDITEG-TDPP        | 5.15 (5.14 ± 0.01) | 1.35                     | 1.09                            | -5.27        | -4.18        |
| TDPP-3TEG-TDPP      | 2.71 (2.71 ± 0.01) | 1.24                     | 1.47                            | -5.24        | -3.77        |
| 2DPP-OD-TEG         | 4.44 (4.42 ± 0.01) | 1.18                     | 1.61                            | -5.34        | -3.73        |

From the calculated dipole moments as shown in Table 2, the side-chain contributes enhancement of the dipole moments for TDPP-3TEG-TDPP and BBT-3TEG-TDPP. Excluding TDPP-3TEG-TDPP, the dipole moments of the other three molecules are in tune with our observed experimental trend of dielectric constants. The low value of the dielectric constant of TDPP-3TEG-TDPP is likely due to the differences in the conformations of the monomer in the polymer unit, which is also partly guided by the possible intermolecular interactions. Another contributing factor could be the presence of disorder, that we have neglected in our present computational studies. A detailed study of this discrepancy will be worth exploring in future.

Energetic disorder plays a larger role in a semiconductor and as it is the manifestation of the density of electronic states, it impacts the device performance significantly. To experimentally determine energetic disorder of all the polymers, we performed photothermal deflection spectroscopy (PDS) to quantitatively estimate the $E_U$ (Figure 4a). The lower the $E_U$, the less the energetic disorder or defect states in the material and hence the voltage loss would be minimized for a photovoltaic cell. Single-component photovoltaic cells were fabricated using inverted architecture as shown in Figure 4b. The $V_{OCS}$ are shown in
Table 2. As evident, the polymers having lower $E_U$ have higher $V_{OC}$ (Table 2). However, the PCEs of the single-component OSCs were of the order of 0.001%. The J-V curves of all the single-component devices are shown in Figure S6.

Table 2. Calculated dipole moments (in the unit of Debye) for the monomers and dimers of the synthesized polymers and the corresponding model systems where the large side chains are replaced by methyl/isopropyl groups.

|          | 2DPP-OD-TEG | TDPP-3TEG-TDPP | BBT-3TEG-TDPP | PNDITEG-TDPP |
|----------|-------------|----------------|---------------|--------------|
| Monomer$^a$ | 0.68        | 5.49           | 5.32          | 2.51         |
| Dimer$^a$  | 1.15        | 11.77          | 11.48         | 3.14         |
| Monomer$^b$ | 0.71        | 0.71           | 0.77          | 1.86         |
| Dimer$^b$  | 1.29        | 1.29           | 0.89          | 2.75         |
| Urbach Energy ($E_U$) (meV) | 68.4        | 75.5           | 57.0          | 116.3        |
| $V_{OC}$ (V) | 0.202       | 0.199          | 0.574         | 0.066        |

$^a$with all the substituents; $^b$model

Figure 4. (a) Photothermal deflection spectra of all the polymers showing tail state absorption; (b) inverted device architecture of single-component organic solar cells.

Exciton dynamics and diffusion length:

To understand the exciton lifetime and diffusion length, transient absorption spectroscopy (TAS) was employed to study polymer thin films. Under photoexcitation, all the polymers exhibit photoinduced absorption (PIA) due to photogenerated excitons as shown in Figure S7. The spectral shapes stay consistent throughout the measurement time window of up to 6 ns, indicating only excitons are present and there is no signal of charge generation. Turning to the kinetics, we fitted the transient kinetics with mono-exponential decay (Figure 5a). Among these materials, BBT-3TEG-TDPP exhibits the longest lifetime of 80 ps, followed
by PNDITEG-TDPP with a lifetime of 12 ps and the rest of the polymers show lifetimes on the order of 5 ps. Using previously described method, the diffusion length was calculated and was found to be the longest for BBT-3TEG-TDPP of 8 nm. Whereas this diffusion length was further reduced to less than 4 nm for the rest of polymers, which therefore limited their performance in photovoltaic devices. The transient absorption kinetics of all the polymers with different fluences are shown in Figure S8. To elucidate if the dielectric constant affects the exciton lifetime, we compared the kinetics between two polymers with the same bandgap but dramatically different dielectric constants, 2DPP-OD-TEG \((\varepsilon_r=4.4)\) and 2DPP-OD-OD \((\varepsilon_r=2.1)\). The chemical structure of 2DPP-OD-OD is shown in Scheme S1. We found that they have similar exciton lifetimes of 5 ps. We further plotted the exciton lifetime of all the polymers against their bandgap as presented in Figure 5b, which shows a linear relationship between the lifetime and bandgap.

![Figure 5](image)

*Figure 5. (a) Normalised transient absorption kinetics for the studied materials. Samples were excited at 700 nm; (b) The plot of exciton lifetime against the band-gap of the studied materials.*

**Conclusion:**

In summary, we report synthesis, dielectric and optical properties of a series of low band-gap conjugated polymers. Multiple TEG side-chains were introduced to enhance the dielectric constant of these polymers. Our studies show that, the combined effect of dipole moment in polymer backbone and side-chain polarization resulted into enhanced \(\varepsilon_r\) for one of the conjugated polymers (BBT-3TEG-TDPP) in low-frequency range. However, single-component OSCs fabricated using these polymers exhibited higher photovoltage for BBT-3TEG-TDPP with minuscule short-circuit current, which suggests that observed
enhancements in photovoltage do not have their origin in dielectric surroundings. TA spectroscopy studies revealed that exciton lifetime and diffusion lengths are long for BBT-3TEG-TDPP. The theoretical calculations of the polymers showed the trend in dielectric properties observed experimentally. This study identifies the important guideline related to molecular design such as substitution of multiple polar side-chains in conjugated polymers enhances the dielectric constant of conjugated polymers. However, it fails to surpass Coulombic attraction between the photogenerated hole and electron. As a further step, increasing the electronic polarization of the polymer backbone may improve the $\varepsilon_r$ in higher frequencies, which may provide desirable environment to dissociate excitons, and more efforts should be made towards designing such conjugated polymers. The GIWAXS results revealed that BBT-3TEG-TDPP and TDPP-3TEG-TDPP are amorphous in nature whereas, 2DPP-OD-TEG and PNDITEG-TDPP have semicrystalline nature. Correlating this with the observed exciton diffusion length of the polymers, we can presume that the crystallinity is not the necessary factor to exhibit larger exciton diffusion length. Understanding the higher exciton diffusion length in amorphous BBT-3TEG-TDPP system would require concerted theoretical and experimental studies which is a part of our further investigation.

**Acknowledgements:**

A.A.M. acknowledges IISc Bangalore for Senior Research Fellowship. This work was performed in part at the SAXS/WAXS beamline at the Australian Synchrotron, Part of ANSTO. A.N. acknowledges support from the Indian Institute of Science start-up grant (SG/MHRD-19-0001). SP acknowledge support from EPSRC project ‘Strategic University Network to Revolutionize Indian Solar Energy-SUNRISE (EP/P032591/1) and Department of Science and Technology, New Delhi for SwarnaJayanti Fellowship.

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Electronic Supplementary Information

Experimental Section

Materials:
All the chemicals were used as received without any further modification. For synthesis of polymers, all the solvents and reagents were purchased from Sigma-Aldrich and used as received. PEDOT:PSS (Clevios PVP AI 4083) was purchased from Heraeus. Anhydrous 1,1,2,2-tetrachloroethane (TCE) and chloroform were purchased from Sigma-Aldrich. Pre-patterned ITO coated glass substrates (12 × 12 × 1.1 mm with 7 mm ITO stripe) were purchased from Colorado Concept Coatings, U.S. Evaporation grade silver was purchased from Sigma-Aldrich.

Methods:
Average molecular weights (Mw, Mn) were determined by Gel permeation chromatography (GPC) against polystyrene standards. THF was used as eluent for PNDITEG-TDPP and Chloroform was used for the other three polymers with a flow rate of 1mL/min. Monomers were synthesized according to the reported methods.

Thermogravimetric analysis (TGA) measurements were conducted on a Mettler Toledo TGA SDTA 851 apparatus at a heating rate of 10°C/min under a nitrogen atmosphere.

Polymer thin films were prepared by spinning their dissolved solutions in chloroform:TCE (1:1) mixture (10 mg/mL) at 1000 rpm on pre-cleaned ozone-treated spectrosil substrates. UV-visible absorption spectra were recorded in transmission mode using PerkinElmer (Lambda 35) spectrometer in ambient conditions. Thin films for atomic force microscopy (AFM) of neat polymers were prepared by dissolving in chloroform:TCE (1:1) mixture followed by spin-coating onto pre-cleaned ozone-treated Si wafers. AFM images for all the blends were recorded by using Oxford instruments Asylum research Cypher S AFM instrument in tapping mode. The thickness of active layers was measured using a Bruker Dektak XT profilometer with a 2 µm tip scanning with 2 mg force.

Cyclic voltammetry (CV) measurements were carried out by drop-casting polymer thin-films from their dissolved solutions on platinum disc electrodes in CHCl₃. 0.1 M Bu₄NPF₆ was used as supporting electrolyte under nitrogen atmosphere at room temperature. Ag/AgCl was used as the reference electrode where platinum rod was employed as both counter electrode and ferrocene/ferrocenium (Fc/Fc⁺) couple as standard.
Devices for impedance spectroscopy measurement were fabricated in ITO/PEDOT:PSS/polymer/Ag architecture. For device fabrication, pre-patterned ITO substrates were cleaned by ultrasonic treatment in soap solution, de-ionized water, acetone and isopropanol, sequentially, for 15 mins each. Then the substrates were dried with N₂ flow, followed by oxygen-plasma treatment for 15 mins. A thin layer (≈30 nm) of PEDOT:PSS was prepared by spin-coating at 5000 rpm for 45 s followed by baking at 180°C for 30 mins under air. The optimized concentration of polymers was 18 mg/mL in 1:1 mixture of chloroform and TCE. The solutions were prepared inside glove box and stirred at 40 °C for 3 hours to ensure complete dissolution. Then, the polymers were spin-coated onto PEDOT:PSS coated ITO substrates at 1000 rpm for 60 s with acceleration of 500 rpm/s. Finally, 100 nm Ag was evaporated onto the polymer coated substrates at the rate of 1 Å/s using a shadow mask, defining the active pixel area of 4.5 mm², in a thermal evaporator at a pressure less than 2x10⁻⁶ Torr.

The room temperature dielectric measurements were carried out in a closed cycle helium cryostat of Cryo Industries Inc using a Keysight E4990A Impedance Analyzer. Silver contacts were made on the thin films (in the device), one on the ITO substrate and another on the deposited Ag film to make it into a capacitive circuit. The pixel area of 4.5 mm² is considered here as the active area common between the two electrodes. Several such pixel area were selected for the experiment to get better estimate of the dielectric constant. The measurements were performed in the frequency range of 100 Hz - 10 MHz at RT with an AC drive voltage of 0.5 V, in the presence of stray light and in the dark condition to nullify the effect of light induced exciton formation. The measurements were also done in the DC bias of -0.5 V and -1.0 V in the dark to cease the effect of electronic charges on the film.

The single-component solar cells were fabricated in inverted architecture (ITO/ZnO/polymer/MoO₃/Ag). On the pre-cleaned ozone-treated ITO substrates, a thin layer (≈30 nm) of ZnO was prepared by spin-coating (at 5000 rpm for 45 s) from a precursor solution of zinc acetate dihydrate (1.00 g) and ethanolamine (0.28 g) in 2-methoxyethanol (10 mL), followed by baking at 200°C for 15 mins under air. The concentration of polymers was fixed at 18 mg/mL in 1:1 mixture of chloroform and TCE. Then, the polymers were spin-coated onto ZnO coated ITO substrates at 1000 rpm for 60 s with acceleration of 500 rpm/s inside the glove box. Finally, 10 nm MoO₃ and 100 nm Ag were sequentially deposited on top.
of the active layer using a shadow mask, defining the pixel area of 4.5 mm$^2$, in a thermal evaporator at a pressure less than 2x10$^{-6}$ Torr.

The photocurrent density-voltage (J-V) characteristics of all the devices were measured in air using a KHS 575 solar simulator with an AM 1.5G spectrum calibrated to 1 sun using a pyranometer.

A broadband pump-probe fs TA spectrometer Helios (Spectra Physics, Newport Corp.) was used to measure the TAS spectra and kinetics for thin film samples. Ultrafast laser pulses (800 nm, 100 fs pulse duration) were generated by using a 1 kHz Ti:sapphire regenerative amplifier (Solstice, Spectra Physics). One portion of the 800-nm pulses was directed to an optical parametric amplifier (TOPAS) to generate the visible pump pulses at 700 nm. The rest of the 800 nm pulses routes onto a mechanical delay stage (6 ns time window) and is directed through a sapphire crystal to generate a white light probe ranging from 800 to 1600 nm in the near-infrared region. The pump and probe beams were focused onto the same spot on the samples. All the samples were encapsulated during the measurements.

Photothermal deflection spectroscopy (PDS) is a scatter-free surface sensitive absorption measurement capable of measuring 5-6 orders of magnitude weaker absorbance than the band edge absorption. For the measurements, a monochromatic Pump light beam is shined on the sample (film on Quartz substrate), which on absorption produces a thermal gradient near the sample surface via nonradiative-relaxation induced heating. This results in a refractive index gradient in the area surrounding the sample surface. This refractive index gradient is further enhanced by immersing the sample in an inert liquid FC-72 Fluorinert® (3M Company) which has a high refractive index change per unit change in temperature. A fixed wavelength CW laser probe beam is passed through this refractive index gradient producing a deflection proportional to the absorbed light at that particular wavelength, which is detected by a photodiode and lock-in amplifier combination. Scanning through different wavelengths gives us the complete absorption spectra. Because this technique makes use of the non-radiative relaxation processes in the sample, it is immune to optical effects like interference and scattering.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) measurements were collected at the small and wide angle X-ray scattering beamline at the Australian Synchrotron. The detector
utilized was a Pilatus 1M active pixel 2D detector with 0.172 mm × 0.172 mm pixels, in integration mode, positioned approximately 400 mm from the sample location. The precise sample-to-detector distance was determined with a silver behenate standard. 15 keV incident X-ray focused to approximately a 0.25 mm × 0.1 mm spot was used to provide large enough q-space. An angle of incidence close to the critical angle was used, chosen as the angle that maximised the scattering intensity. The 2D raw data was reduced and analysed with a modified version of Nika.\textsuperscript{51}

**Synthetic procedure for Poly BBT-3TEG-TDPP:**

3,6-bis(5-bromothiophen-2-yl)-2-(2-ethylhexyl)-5-((1-(3,4,5-tris(2-(2-methoxyethoxy)ethoxy)ethoxy)benzyl)-1H-1,2,3-triazol-4-yl)methyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (3TEGTDP-Br\textsubscript{2}) was synthesized using reported procedure.\textsuperscript{42} (4,8-bis(5-(2-ethylhexyl)thiophen-2-yl)benzo[1,2-b:4,5-b']dithiophene-2,6-diyl) bis (tributylstannane) (BBT (SnBu\textsubscript{3})\textsubscript{2}) was synthesized using literature reported procedure.\textsuperscript{52} 3TEGTDP-Br\textsubscript{2} (0.2 g, 0.16 mmol) and BBT (SnBu\textsubscript{3})\textsubscript{2} (0.18 g, 0.16 mmol) were taken in degassed dry toluene (20 mL) and two drop of aliquot 336 were added. The reaction container was loaded with catalyst Pd(PPh\textsubscript{3})\textsubscript{4} (10 mg). This mixture was maintained at 100 °C for 48h. Then cooled to room temperature and quenched with 1M HCl (10 mL) and then washed with EDTA solution, extracted with chloroform and dried over anhydrous Na\textsubscript{2}SO\textsubscript{4}, the organic layer was evaporated, and concentrated solution was precipitated by methanol. Dark green precipitated was collected by filtration and then washed with hot methanol and hexane by soxhlet extraction to remove unreacted starting materials and lower molecular weight oligomers. The product was dried under vacuum to obtain pure BBT-3TEG-TDPP as a dark green solid (0.18 g, 68%).
Figure S1. $^1$H NMR spectrum of BBT-3TEG-TDPP in CDCl$_3$.

Synthetic procedure for Poly TDPP-3TEG-TDPP:

2,5-bis(2-octyldodecyl)-3,6-bis(5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophen-2-yl) pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (TDPP(BE)$_2$) was synthesized using the procedure laid down by Catherine et al.$^{40}$ 3TEGTDP-P-Br$_2$ (0.2 g, 0.16 mmol) and TDPP(BE)$_2$ (0.18 g, 0.16 mmol) were taken in degassed dry toluene (20 mL) and two drop of aliquat336 were added. The reaction container was loaded with ligand (o-tol)$_3$P (15 mg), catalyst Pd$_2$(dba)$_3$ (10 mg) and purged with argon for 10 min to remove dissolved oxygen and was added aqueous (1 mL) solution of degassed K$_3$PO$_4$ (44 mg, 0.3 mmol). This mixture was refluxed at 110 °C for 48 h. Then cooled to room temperature and quenched with 1M HCl (10 mL) and then washed with EDTA solution, extracted with chloroform and dried over anhydrous Na$_2$SO$_4$, the organic layer was evaporated, and concentrated solution was precipitated by methanol. Dark green precipitated was collected by filtration and then washed with hot methanol and hexane by soxhlet extraction to remove unreacted starting materials and lower molecular weight oligomers. The product was dried under vacuum to obtain pure TDPP-3TEG-TDPP as a dark green solid (0.2 g, 64%).
Figure S2. $^1$H NMR spectrum of TDPP-3TEG-TDPP in CDCl$_3$.

**Synthetic procedure for Poly PNDITEG-TDPP:**

$$(((4,9\text{-dibromo-1,3,6,8-tetraoxobenzo[imn][3,8]phenanthroline-2,7(1H,3H,6H,8H)-diyl}) \text{bis(ethane-2,1-diyl})bis(oxy)})\text{bis(ethane-2,1-diyl}) \text{bis(2-(2-(2-methoxyethoxy)ethoxy)acetate}) \text{(NDITEG-Br}_2 \text{)}$$

was synthesized using literature reported procedure.\textsuperscript{41} NDITEG-Br$_2$ (0.2 g, 0.2 mmol) and [TDPP(BE)$_2$] (0.24 g, 0.2 mmol) were taken in degassed dry toluene (20 mL) and two drop of aliquat336 were added. The reaction container was loaded with ligand (o-Tol)$_3$P (15 mg), catalyst Pd$_2$(dba)$_3$ (10 mg) and purged with argon for 10 min to remove dissolved oxygen and was added aqueous (1 mL) solution of degassed K$_3$PO$_4$ (55mg, 0.4 mmol). This mixture was refluxed at 110 °C for 48 h. Then cooled to room temperature and quenched with 1M HCl (10 mL) and then washed with EDTA solution, extracted with chloroform and dried over anhydrous Na$_2$SO$_4$, the organic layer was evaporated, and concentrated solution was precipitated by methanol. Dark green precipitated was collected by filtration and then washed with hot methanol and hexane by Soxhlet extraction to remove unreacted starting materials and lower molecular weight oligomers. The product was dried under vacuum to obtain pure PNDITEG-TDPP as a dark green solid (0.15 g, 42%).
Figure S3. $^1$H NMR spectrum of Poly PNDITEG-TDPP in CDCl$_3$.

Table S1. Molecular weight of polymers determined using gel-permeation chromatography (GPC) using polystyrene as standard.

| Polymers          | $M_n$ (kDa) | $M_w$ (kDa) | PDI |
|-------------------|-------------|-------------|-----|
| PNDITEG-TDPP      | 78.23       | 292.15      | 3.73|
| BBT-3TEG-TDPP     | 12.77       | 38.07       | 2.98|
| TDPP-3TEG-TDPP    | 13.71       | 33.61       | 2.45|
| 2DPP-OD-TEG       | 25.40       | 77.62       | 3.06|
Figure S4. Cyclic voltammograms of (a) 2DPP-OD-TEG (b) BBT-3TEG-TDPP (c) TDPP-3TEG-TDPP and (d) PNDITEG-TDPP and ferrocene (dotted line in (a)) obtained using three electrode-system with Ag/AgCl as reference electrode and Bu$_4$NPF$_6$ in acetonitrile as electrolyte. 2DPP-OD-TEG, 3TEG-TDPP exhibit one and two-step reduction, respectively, whereas, 3TEG-BBT and PNDITEG-TDPP exhibit three-step reduction. However, BBT-3TEG-TDPP exhibits three-step oxidation but TDPP-3TEG-TDPP, PNDITEG-TDPP and 2DPP-OD-TEG exhibit one-step oxidation. (e) HOMO and LUMO energy levels of all the polymers were estimated using the onset reduction and oxidation potentials from CV, PNDITEG-TDPP has the deepest lying LUMO and lowest electrochemical bandgap.
Figure S5. Capacitance vs. frequency plots of (a) PNDITEG-TDPP, (b) BBT-3TEG-TDPP, (c) TDPP-3TEG-TDPP and (d) 2DPP-OD-TEG in light, dark, under -0.5 V and -1 V DC bias. The convergence of capacitance to the geometric value is evident in higher frequencies showing the depletion of photogenerated charge carriers for all the polymers.
Figure S6. Current-voltage characteristics of all the polymers measured under AM 1.5G conditions.

Figure S7. IR TA spectra for the four polymer thin films. The pump wavelength was 700 nm.
To understand the role of microstructures and the effect of packing, we performed atomic force microscopy (AFM) and grazing incidence wide angle X-ray spectroscopy (GIWAXS) on the neat polymer films. The AFM images show smooth films for all the polymers (Figure S9).

To understand the molecular packing and crystallinity of the polymers in solid state, we
performed GIWAXS studies. From the 2D GIWAXS plot of all the four polymers in Figure S10, it is evident that the TDPP-3TEG-TDPP and BBT-3TEG-TDPP are weakly crystalline as indicated by the broad, diffuse diffraction rings. 2DPP-OD-TEG shows stronger lamellar stacking, labelled (100), with diffraction up to third order apparent. The lamellar stacking peak of 2DPP-OD-TEG is located at q value of 0.298 Å⁻¹ corresponding to a d-spacing of 21.1 Å. At higher q, 2DPP-OD-TEG exhibits a (010) peak at q value of 1.74 Å⁻¹ which corresponds to a π-π stacking distance of 3.61 Å. PNDITEG-TDPP also exhibits semi-crystallinity although it is not as ordered as 2DPP-OD-TEG. A lamellar stacking peak for PNDITEG-TDPP is seen at q = 0.315 Å⁻¹ corresponding to d-spacing of 19.9 Å, which is a tighter lamellar stacking compared to 2DPP-OD-TEG. PNDITEG-TDPP does not exhibit a distinct π-π stacking peak but does show a pronounced (001) backbone reflection suggesting a relatively rigid backbone stacking which is expected because of more planar backbone. The backbone stacking peak is located at a q value of 0.715 Å⁻¹ corresponding to d-spacing of 8.78 Å. However, these results could not be correlated with the observed highest exciton diffusion length of BBT-3TEG-TDPP.

Figure S9. AFM height images of (a) PNDITEG-TDPP, (b) BBT-3TEG-TDPP, (c) TDPP-3TEG-TDPP, (d) 2DPP-OD-TEG; and phase images of the same in same order from e-h.
Figure S10. (a, c, e, g) 2D GIWAXS patterns and 1D line profiles (b, d, f, h) taken of PNDITEG-TDPP (a, b), BBT-3TEG-TDPP (c, d), TDPP-3TEG-TDPP (e, f), and 2DPP-0D-TEG (g, h).
Theoretical Calculations:

Optimized geometries and coordinates of the molecules 2DPP-OD-TEG, 3TEG-TDPP, 3TEG-BBT and PNDITEG-TDP, corresponding model systems where the large side chains are substituted by methyl/Isopropyl groups and the corresponding dimers calculated at B3LYP/6-31g(d) level of theory. All the structures are minima on the potential energy surface.
