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New low bandgap near-IR conjugated D-A copolymers for BHJ polymers solar cell applications


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Abstract

We synthesized two novel ultra low bandgap donor-acceptor (D-A) copolymers ($E_g \leq 1.2$ eV), containing the thiazoloquinoxaline unit as the main electron accepting unit (A) and benzodithiophene (BDT) and dithienosilole (DTS) as different donor units (D), denoted as $P_1$ and $P_2$, respectively, by cross-coupling Stille reaction. The copolymers possess a light absorption range from UV (350 nm) to near-IR (1300 nm) with optical bandgaps 1.16 eV and 1.08 eV, respectively. Comparison between quantum-chemical calculations with experimental data were performed for proposing more detailed conception of the optical and electronic properties of these copolymers and used a donor for polymer solar cells (PSCs). The PSCs based on optimized $P_1$:PC$_{71}$BM and $P_2$:PC$_{71}$BM showed overall power conversion efficiency (PCE) of 4.32 % and 3.48 %, respectively. Although the $P_2$ possess broad absorption coverage up to 1300 nm, the lower PCE may be attributed to the low $J_{sc}$, due to the poor driving force for exciton dissociation, since the LUMO offset with PC$_{71}$BM is less than 0.3 eV. The PCE has been significantly increased to 7.27 % and 6.68 % for solvent vapor annealing (SVA) treated $P_1$:PC$_{71}$BM and $P_2$:PC$_{71}$BM active layers, respectively. This improvement arises from the appropriate nanoscale morphology and increase in hole mobility, induced by SVA treatment of the active layer.

Key words: NIR copolymers, Bulk heterojunction solar cells, solvent vapor annealing, power conversion efficiency

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Introduction

Polymer solar cells (PSCs) based on bulk heterojunction active layer (blend of polymer as electron donor and fullerene derivatives as electron acceptor) have attracted a lot of attention due to their exclusive advantages in combining lightweight, flexible and large area devices at low cost of fabrication [1]. A record power conversion efficiency (PCE) of around 10 % for single layer BHJ [2] and 11 % for tandem solar cells [3] have been achieved in recent years with the molecular engineering of new low bandgap donor materials. An ideal polymer donor material for PSCs should possess a broad band absorption covering from visible to near infrared region of solar spectrum to achieve a high short circuit current, suitable frontier energy levels matching with the fullerene acceptor to attain a high open circuit voltage, sufficient solubility to assure solution process ability to form nanoscale bicontinuous network and high hole mobility for efficient charge transport.

In recent years low bandgap polymeric materials absorbing light up to near-IR range have been of great interest for polymeric solar cells (PSC), photo-sensors and field effect transistors (FET) [4]. Using near-IR photovoltaic polymeric materials may expand light absorption up to the near-IR and even beyond a 1000 nm range that could possibly enhance PCE of the PSCs. Although conjugated ultra low bandgap polymers were synthesized earlier [5], design and synthesis of the polymers absorbing light beyond 900 nm range with neatly regulated energy levels and considerable PCE in polymer : fullerene PSC are highly demanded. D-A polymers with strictly alternating strong electron-accepting and strong electron-donating construction blocks are generally used for the fabrication of ultra low bandgap polymers and are highly required for photon absorption in the long wavelength solar spectrum range where high photon flux exists. Assuming that the transparent electrode possesses 85% transmittance of standard solar spectrum (AM 1.5G), then the PSC’s theoretical maximum short circuit current density ($J_{sc}$) would be 14.3 mA/cm$^2$ in 300-650 nm range. If one expands the photocurrent response to 1000 nm, then the maximum short circuit current density would be increased up to 31.9 mA/cm$^2$ [6]. These simple calculations clearly demonstrate that the absorption spectrum has significant effects on the photovoltaic characteristics especially $J_{sc}$. NIR-polymers absorb a significant fraction of solar light that makes it possible to obtain $J_{sc}$ higher 30 mA/cm$^2$. In recent years a number of infrared absorbing polymers for PSC applications have been reported. However, all of these NIR-polymers were found to have efficiency lower than 1% PSC [7] which is due to low incident photon to current conversion efficiency (IPCE) values in the near-IR spectral range.
Nevertheless, Wong et al. have developed single-junction NIR-polymers based PSC with a high efficiency of 6% [8]. Also, it was recently reported that a tandem device based on medium bandgap and NIR conjugated polymers as one of the donor polymers reached high efficiency of 10% [9]. These recent efforts inspired us to develop novel NIR-absorbing polymers for PSC applications. To obtain D-A NIR polymers strong electron-donor and strong electron-acceptor structures need to be used. Generally, strong electron donor monomers include pyrrole, thiophene, ethylene-di-oxy-thiophene, benzodithiophene (BDT), bi-thiophene derivatives, di-thienosilole (DTS) etc. Among them BDT and DTS units possess symmetric and rigid planar structure with enhanced π-conjugation. Usually BDT and DTS based polymers exhibit a broad absorption range, high charge carrier mobility and low-lying HOMO compared to polymers based on other electron-donating units. On the other hand, most prominent electron-deficient units used for D-A NIR polymer design are diketopyrrolopyrrole [10], benzobisthiadiazole [11], pyrazinoquinoxaline [12], benzotriazole, thienoisoindigo [13] etc.

In our effort to develop novel D-A NIR-absorbing polymers we started from thiaiazoloquinoxaline (TDAZQ) derivatives as the central strong accepting unit due to its rigid planar structure and presence of four imino groups with such unique properties as high charge carrier mobility, intensive spectral absorption up to IR range and ease of functionalization with various aryl- and alkyl- groups for solubility improving. Despite that TDAZQ-based conjugated polymers were used in PSC, only a limited number of structures with ultra low bandgap ($E_g < 1.4$ - $1.5$ eV) have been presented up to date. They are highly demanded and studied relatively limited [1b].

In this manuscript two novel low bandgap D-A copolymers with the same TDAZQ as strong acceptor and alternating with different BDT and DTS as electron donors, denoted as $P_1$ and $P_2$, respectively, were designed and synthesized in cross-coupling Stille reaction. Optical, electrochemical and PSC characteristics of the obtained polymers were investigated systematically. The new synthesized copolymers possess broad (panchromatic) absorption spectra in 300-1300 nm range with optical bandgaps below 1.2 eV. These copolymers were used as donor materials along with PC$_{71}$BM as acceptor for solution processed BHJ PSCs. PSCs with bulk heterojunction based on optimized $P_1$:PC$_{71}$BM and $P_2$:PC$_{71}$BM blends cast from chloroform solution demonstrate over all PCE of efficiency of 4.32 and 3.48 %, respectively. The PCE has been further improved up to 7.27 % and 6.68 % for solvent vapor annealing (SVA) treated $P_1$:PC$_{71}$BM and $P_2$:PC$_{71}$BM active layers, respectively.

Experimental section
Synthesis

All the starting materials and reagents were purchased from commercial sources and used without further purification, unless otherwise noted. All reaction involving air-sensitive reagent were performed under a nitrogen atmosphere. 2,6-bis(trimethylthio)-4,8-bis(dodecyl)benzo[1,2-b;3,4-b']dithiophene monomer (M1) [14], 2,2'-bistrimethylstannyl-4,4'-bis-(2-ethylhexyl)-dithieno[3,2-b:2',3'-d]silole (M2) [15] and brominated monomers 8,12-bis(5-bromo-4-dodecylthiophen-2-yl)-2,5-di(nonadecan-3-yl) [1,2,5] thiadiazolo [3,4-i]bis[1,3] thiazolo[4,5-a:5',4'-c]phenazine (M3) [16] are prepared according to the known literature procedures.

Synthesis of Poly {4,8-didodecyloxybenzo[1,2-b;3,4-b'] dithiophene -8,12-bis (4-dodecylthiophen-2-yl) -2,5-di(nonadecan-3-yl)[1,2,5] thiadiazolo[3,4-i] bis[1,3] thiazolo[4,5-a:5',4'-c]phenazine}(P1): 8,12-bis(5-bromo-4-dodecylthiophen-2-yl)-2,5-di(nonadecan-3-yl) [1,2,5] thiadiazolo [3,4-i]bis[1,3] thiazolo[4,5-a:5',4'-c]phenazine (0.7721 g, 0.5 mmol) compound M3, 2,6-bis-trimethylstannyl-4,8-didodecyloxybenzo[1,2-b;4,5-b']dithiophene M1 (0.4423 g, 0.5 mmol), Pd(Ph₃P)₄ (0.027 g, 0.0234 mmol) and toluene (18 ml) were heated under argon at 110˚C for 48 h. After cooling to r.t. reaction mixture was poured into methanol (200 ml) and filtrated. Polymer was dissolved in CHCl₃ and precipitated with methanol. Then it was purified by extraction with methanol, hexane and chloroform in Soxlet apparatus. Polymer was recovered as a solid from the chloroform fraction by precipitation from methanol, filtered off, and dried under vacuum to obtain as black solid Yield 81%. Calc. for C₁₁₈H₁₈₂N₆S₇, %: C, 74.23; H, 9.60; N, 4.40; S, 11.76. Found: C, 73.86; H, 9.28; N, 3.95; S, 11.21. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 9.50(s,2H), 7.75(s,2H), 4.43 (m,4H), 3.42(m,2H), 3.21(m,4H), 2.25-0.70(m,168H).  Mₙ = 10400, Mₘ = 20200, PDI=1.94

Synthesis of poly(4,4'-bis(2-ethylhexyl) dithieno[3,2- b :2',3'- d ]silole-8,12-bis(4-dodecylthiophen-2-yl)-2,5-di(nonadecan-3-yl)[1,2,5] thiadiazolo[3,4-i]bis [1,3thiazolo[4,5-a :5',4'- c] phenazine) (P2): P2 was prepared similarly as P1 using 8,12-bis(5-bromo-4-dodecylthiophen-2-yl)-2,5-di(nonadecan-3-yl) [1,2,5] thiadiazolo [3,4-i]bis [1,3] thiazolo[4,5-a:5',4'-c]phenazine compound (M3) and 2,2'-bistrimethylstannyl-4,4'-bis-(2-ethylhexyl)-dithieno [3,2-b:2',3'-d]silole (M2) with 66% yield. Calc. for C₁₀₈H₁₆₆N₆S₇Si, %: C, 72.02; H, 9.30; N, 4.67; S, 12.46; Si, 1.56. Found: C, 71.53; H, 9.18; N, 4.24; S, 12.04. ¹H NMR (400 MHz, CDCl₃, δ, ppm): 9.38(s,2H), 7.50(s,2H), 3.50 (m,2H), 3.15(m,4H), 2.25-0.70(m,156H).  Mₙ = 8300, Mₘ = 13000, PDI=1.57
NMR \(^1\)H and \(^{13}\)C spectra of the starting compounds and polymers were recorded on the spectrometer "Bruker Avance-400" with a working frequency of 400.13 and 100.62 MHz, respectively. IR spectra were recorded by FT-IR spectrometer "Perkin - Elmer 1720-X", TGA analysis was performed on "Perkin-Elmer TGA-7" with heating rate 20 deg/min. Average molecular weights and polydispersity analysis was performed on the GPC instrument company "Waters", consisting of a pump M-600, two columns U-Styrargel Linear, spectrophotometric detector M-484 and data acquisition and processing system Maxima Transmission electron microscopy (TEM) images were recorded with a Tecnai G2F30 transmission electron microscope (FEI Inc.; accelerating voltage = 300 kV).

**Fabrication and characterization of polymer solar cells**

The PSCs were fabricated in a conventional structure i.e. ITO/PEDOT:PSS/P1 or P2:PC\(_{71}\)BM/Al. First of all, indiums tin oxide (ITO) coated glasses were cleaned by sequential ultrasonic treatment in detergent, deionized water, acetone and isopropanol for 20 min and dried in ambient conditions. Than, a thin layer (35 nm) PEDOT:PSS (poly(3,4-ethylene dioxythiophene): poly(styrenesulfonate)) was spin coated at 3500 rpm for 40 s on the ITO coated glass substrate and subsequently baked at 120° C for 15 min in air. The copolymers and PC\(_{71}\)BM (total concentration of 20 mg/mL) in different weight ratios were dissolved in chloroform and spin coated at 2000 rpm for 1 min on top of the PEDOT:PSS layer. For the solvent vapor annealing (SVA), the active layer was kept in a glass petri dish containing 200 \(\mu\)L THF for 20 min at room temperature. The average thickness of the active layer was about 90 nm. A cathode consisting of Ca (10 nm) capping with aluminum (~30 nm) was deposited by thermal evaporation under a shadow mask with base pressure less than 10\(^{-5}\) torr, on top of the active layer. The active area of the devices was ~20 mm\(^2\). The current–voltage characteristics of the BHJ organic solar cells were measured using a computer controlled Keithley1238 source meter under simulated AM1.5G, 100 mW/cm\(^2\). A xenon light source coupled with optical filter was used to give the stimulated irradiance at the surface of the devices. The incident photon to current efficiency (IPCE) of the devices was measured illuminating the device through the light source and monochromator and the resulting current was measured using a Keithley electrometer under short circuit condition.

The hole-only devices with ITO/PEDOT:PSS/active layer/Au were also fabricated in an analogous way, in order to measure the hole and electron mobility, respectively.

**Results and discussion**

**Synthesis and characterization**
The synthetic routes of the targeted $P_1$ and $P_2$ copolymers are described in Scheme 1. The copolymers $\text{poly}\{4,8\text{-didodecyloxybenzo}[1,2-b;3,4-b] \text{dithiophene}-8,12\text{-bis}(4\text{-dodecylthiophen}-2\text{-yl})-2,5\text{-di(nonadecan}-3\text{-yl})[1,2,5] \text{thiadiazolo}[3,4- \text{i}] \text{bis}[1,3] \text{thiazolo}[4,5- \text{a}:5',4'\text{c}] \text{phenazine} \}$ ($P_1$) and $\text{poly}(4,4'\text{-bis}(2\text{-ethylhexyl}) \text{dithieno}[3,2-b;2',3'-d] \text{silole}-8,12\text{-bis}(4\text{-dodecylthiophen}-2\text{-yl})-2,5\text{-di(nonadecan}-3\text{-yl})[1,2,5] \text{thiadiazolo}[3,4- \text{i}] \text{bis}[1,3\text{thiazolo}[4,5- \text{a}:5',4'\text{c}] \text{phenazine} \}$ ($P_2$) were prepared via Palladium catalyzed Stille coupling reaction between $2,6\text{-bis}(\text{trimethylthiin})-4,8\text{-bis}(\text{dodecyl})\text{benzo}[1,2-b;3,4-b']\text{dithiophene monomer} \ (M_1)$ (or $2,2'\text{-bistrimethylstannyl}-4,4'\text{-bis}(2\text{-ethylhexyl})\text{dithieno}[3,2-b;2',3'-d]\text{silole} \ (M_2)$ and brominated monomers $8,12\text{-bis}(5\text{-brom-4-dodecylthiophen}-2\text{-yl})-2,5\text{-di(nonadecan}-3\text{-yl}) \ [1,2,5] \text{thiadiazolo}[3,4- \text{i}] \text{bis}[1,3] \text{thiazolo}[4,5- \text{a}:5',4'\text{c}] \text{phenazine} \ (M_3)$ with yields ranging from 81% to 66%.

After polymerization, crude polymers were washed using Soxhlet extraction with methanol, hexane and chloroform in sequence. The title polymers were obtained by reprecipitation of their concentrated chloroform solutions from methanol. Both $P_1$ and $P_2$ can be readily dissolved in common solvents such as chloroform, chlorobenzene, and tetrahydrofuran, which is attributed to the incorporation of solubilizing alkyl chains adjoined to thiophene flank of polymer backbone. The structures of the obtained copolymers were confirmed by elemental analysis, $^1\text{H NMR}$ and UV-Vis spectroscopy. $^1\text{H NMR}$ spectrum of $P_1$ and $P_2$ in CDCl$_3$ is shown in Figure 1. The peaks at $7.30-9.60$ ppm are assigned to the proton response of aromatic units. There is a peak at $\delta \ 4.50-3.00$ ppm which is attributed to methylene group (c, d, e) (Figure 1). The peaks in the ranges of $\delta \ 1.90-0.77$ ppm arise from alkyl substituent. All of the integral ratios of peak areas between the aromatic and aliphatic signals agree with corresponding molecular structure of the polymers.

The molecular weight and polydispersity index (PDI) of the polymers were measured by gel permeation chromatography (GPC) using polystyrene as the standard and THF as the eluent. The molecular weights and thermal properties of the $P_1$ and $P_2$ are summarized in Table 1. The GPC results indicated that these copolymers have the number-average molecular weights ($M_n$) of 10.4 and 8.3 kDa with a narrow PDI of 1.94 and 1.57 for $P_1$ and $P_2$, respectively. The thermal properties of polymers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA) (Figure 2). Decomposition temperatures ($T_d$) (5% weight loss) were 335°C and 408°C for $P_1$ and $P_2$, respectively. This indicated that the thermal stability of the copolymers is enough for PSCs applications.
Optical and electrochemical properties

The optical properties of the two copolymers were measured by UV-Vis spectroscopy both in chloroform solutions and in the thin films. The normalized UV-Vis absorption spectra of \( \text{P1} \) and \( \text{P2} \) in chloroform solutions and in solid state are presented in Figure 3, and the corresponding optical properties are summarized in Table 2. Both copolymer films show two main absorption bands in the wavelength range of 350 - 650 nm and 750-1300 nm, corresponding to the \( \pi-\pi^* \) transition of the conjugated backbone and intermolecular charge transfer (ICT) between donor and acceptor units, respectively [17]. As can be seen from Figure 3 that the absorption peak corresponding to ICT band in thin film for both copolymers red shifted as compared to that in solution, indicating strong \( \pi-\pi \)-stacking and polymer main chain aggregation occurred in the films. The ICT band for \( \text{P2} \) in both solution and thin film is redshifted as compared to \( \text{P1} \) due to the enhanced planarity and expanded conjugation due to the DTS. The optical band gaps \( (E_{\text{g}}^{\text{opt}}) \) of \( \text{P1} \) and \( \text{P2} \) were estimated to be 1.16 eV and 1.08 eV, respectively, deduced from the absorption edges of the corresponding thin film absorption spectra, according to expression, \( E_{\text{g}}^{\text{opt}} = 1240/\lambda_{\text{onset}} \). The TDAZQ based polymers show an extended absorption towards the near-infrared region (beyond 1200 nm). However, both polymers show a weak absorption in 590-700 nm region of the active solar spectrum, which may result in the low photon harvesting in PSCs but may be compensated by the absorption spectra of PC\(_{71}\text{BM}\) due to its strong absorption covering from 350 to 750 nm, when a blend of these copolymers with PC\(_{71}\text{BM}\) used as active layer.

The LUMO and HOMO energy levels of both copolymers were evaluated by cyclic voltammetry (CV) of the thin films. The reduction and oxidation curves of the copolymers are shown in Figure 4 and the corresponding electrochemical data are summarized in Table 2. From the CV measurement, both clear oxidation peak and reduction peak were observed for the \( \text{P1} \) and \( \text{P2} \) polymers. HOMO and LUMO level of the polymers were calculated from the onsets of the oxidation \( (E_{\text{onset}}^{\text{ox}}) \) and reduction \( (E_{\text{onset}}^{\text{red}}) \) peak, respectively, while the potentials are determined using ferrocene \( (F_c) \) as standard according following equations:

\[
E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} - E_{F_c/F_c^+}^{1/2} - 4.8)eV
\]

\[
E_{\text{LUMO}} = -(E_{\text{red}}^{\text{onset}} - E_{F_c/F_c^+}^{1/2} - 4.8)eV
\]

\[
E_{g}^{\text{elec}} = (E_{\text{HOMO}} - E_{\text{LUMO}})eV
\]

The potential of ferrocene \( E_{F_c/F_c^+}^{1/2} = 0.40 \) eV) vs. SCE is used as an internal standard. Accordingly, the HOMO energy levels were calculated to be -5.34 eV for both \( \text{P1} \) and \( \text{P2} \),
which are in good agreement with the ideal HOMO energy levels to ensure good air stability and high open circuit voltage ($V_{oc}$) in PSCs [18]. Deep HOMO energy levels of copolymers were desired for achieving a higher $V_{oc}$ in the BHJ PSCs and made these copolymers promising candidates for use as polymer donor materials. It is obvious that the HOMO energy levels of the two polymers are identical due to the presence of the same backbone, which is dependent upon the donating units. The LUMO levels were thus calculated to be -3.88 eV and -3.94 eV for P1 and P2, respectively, which provides a LUMO offset of 0.32 and 0.26 eV between the P1 and P2 and PC71BM (LUMO ~ -4.2 eV), respectively. This offset is very close to 0.30 eV which is generally accepted as the minimum driving force for efficient exciton separation into free charge carriers [19]. Recently, it was found that charge separation also occurs when the LUMO offset is below 0.30 eV [20], indicating that these copolymers can be used as an electron donor for PSCs. The electrochemical band gaps ($E^{\text{elec}}_g$) are 1.46 and 1.40 eV for P1 and P2, respectively, which is close to the ideal band gap for PSC donor materials. The difference between the optically and electrochemically measured energy gaps can be explained by the exciton binding energy of the conjugated copolymers. This result shows that extension of π-conjugation of TDAZQ is a viable strategy to obtain stronger acceptors, with lower band gap, and the copolymers thus possessing deep LUMO and HOMO levels.

**Theoretical calculations**

We have additionally performed a theoretical study on the P1 and P2 molecular structures within the framework of density functional theory (DFT) and time-dependent density functional theory (TD-DFT). The initial geometry optimization calculations were performed employing the gradient corrected functional PBE [21] of Perdew, Burke and Ernzerhof. The def-SVP basis set [22] was used for all of the calculations. At this stage of the calculations, to increase the computational efficiency (without loss in accuracy), the resolution of the identity method [23] was used for the treatment of the two-electron integrals. Subsequent geometry optimization were further performed using the hybrid exchange–correlation functional B3LYP [24] as well as Truhlar’s meta-hybrid exchange–correlation functional M06 [25], and the same basis set. Tight convergence criteria were placed for the SCF energy (up to $10^{-7}$ Eh) and the one-electron density (rms of the density matrix up to $10^{-6}$) as well as for the norm of the Cartesian gradient (residual forces both average and maximum smaller than 1.5x10^-5 a.u.) and residual displacements (both average and maximum smaller than 6x10^-5 a.u.). Solvent effects were included for chloroform (CF).
using the integral equation formalism variant of the Polarizable Continuum Model (IEFPCM), as implemented in the Gaussian package [26].

TD-DFT excited state calculations were performed to calculate the optical gaps of the P1 and P2 using the same functionals and basis set on the corresponding ground state structures. The UV/Vis spectra were calculated using the B3LYP and M06 functionals. Initially, the geometry optimizations were performed using the Turbomole package [27]. All of the follow up calculations were performed using the Gaussian package [26].

The first round of calculations was the geometry optimizations of the P1 and P2 structures. To increase the computational efficiency the alkyl groups were truncated to ethyl groups. Vibrational analysis on all of the optimized structures did not reveal any vibrational modes with imaginary eigen-frequencies, i.e. the final optimized structures are true local (if not global) minima. The structures are not planar with the thiophene moieties forming dihedral angles in the range of 42°–51° (depending on the functional and the presence of solvents with the TDAZQ moiety, and in the range 18°–24° with the BDT moiety (for P1) and 29°–30° with the DTS moiety (for P2). We have calculated the HOMO and LUMO energy levels and the optical gaps, defined here as the energetically lowest allowed vertical electronic excitation, employing the PBE, M06, and B3LYP functionals. In Table 3 in addition to the frontier orbitals’ energy levels, we also provide the optical gap the main contributions to the first excitation as well as the wavelength of the first excitation and of the excitations with the largest oscillator strengths.

In addition to the B3LYP functional we have also performed our calculations employing the M06 functional. The M06 meta-hybrid functional was chosen since it provides leveled performance over transition types [28, 29]. We provide results using all three functionals, which can additionally be used for comparison with the literature.

The HOMO–LUMO (HL) gap of each structure calculated using the hybrid B3LYP functional is notably smaller, by ~ 0.4 eV, than that using the meta-hybrid M06 functional, however, the calculated optical gaps are only marginally smaller, with a difference ~ 0.1 eV. In Table 3 we also provide the character of the first allowed excitations only for contributions larger than 4%. The first excitation, as calculated by each of the functional for all three structures, clearly exhibits a single-configuration character. In Figure 5 we have plotted the iso-surfaces (isovalue=0.02) of the HOMO and LUMO for P1 and P2. For both of the structures the HOMO extends over the main body. For the LUMO of each structure the delocalizations are qualitatively different. The LUMO of both P1 and P2 extends mainly TDAZQ moiety and only minimally over linking thiophenes. The contributions of the
PDOSs for $\textbf{P1}$ and $\textbf{P2}$ are shown in Figure S1 (supplementary information). We partition all of the structures into the linking thiophenes, the moiety and aliphatic groups for both structures, and additionally to BTD for $\textbf{P1}$ and DTS for $\textbf{P2}$. Both structures have high contributions to the HOMO from the TDAZQ moiety, specifically at 60.3% for $\textbf{P1}$ and at 53.7% for $\textbf{P2}$. The linking thiophenes also have high contributions to the HOMO, at 24.0% for $\textbf{P1}$ and at 25.6% for $\textbf{P2}$, which results in an extensive delocalization along the main chain of the structure. The situation is different for the LUMO of the structures, which in both cases extends almost exclusively over the TDAZQ moiety, at 88.1% for $\textbf{P1}$, and at 88.6% for $\textbf{P2}$. Only moderate contributions are noted from the BDT moiety to the HOMO of $\textbf{P1}$ which is at 14.3%, and of the DTS moiety to the HOMO of $\textbf{P2}$ which is at 19.4%. The remaining minor contributions are from the linking thiophene moieties at 9.6% for $\textbf{P1}$, and 9.2% for $\textbf{P2}$. These are in agreement with our earlier observations on the orbital delocalizations.

In Figure 6 we show the UV/Visual absorption spectra of the $\textbf{P1}$ and $\textbf{P2}$ structures calculated at the TD-DFT/M06 level of theory, both accounting for solvent effects for CF and in gas phase. The spectra have been produced by convoluting Gaussian functions with HWHM = 0.18 eV centered at the excitation wavenumbers. In Figure S2 (see Supporting Information) we also provide the corresponding spectra calculated using the B3LYP functional, which is in good agreement with the spectra using the M06 functional, and only slightly overestimate in the long wavelength region by ~35 nm and in the short wavelength region ~15 nm. The calculated absorption spectra of $\textbf{P1}$ and $\textbf{P2}$ have significant similarities; they exhibit three main bands of high absorbance; one centered at large wavelengths ~800 nm, as well as two at low centered at smaller wavelengths at 320 nm and 420–440 nm. Additional low intensity peaks are also noticeable at the smaller wavelengths regions. In the Supporting Information we provide all of the high intensity peaks with the corresponding oscillator strengths (table S1 and S2).

**Photovoltaic properties**

PSCs were fabricated by spin coating the mixture of $\textbf{P1}$ or $\textbf{P2}$ with PC$_{71}$BM from chloroform solution. The active layer was sandwiched between transparent ITO/PEDOT:PSS and Al electrodes. Initially, we examined the different $\textbf{P1}$ or $\textbf{P2}$/PC$_{71}$BM weight ratios to optimize the weight ratio and the best photovoltaic performance was obtained with a blend weight ratio of 1:2 cast from CF solution. Figure 7a shows the current–voltage characteristics under illumination and the related photovoltaic parameters are summarized in table 4. As shown in Figure, the $\textbf{P1}$:PC$_{71}$BM device showed a PCE of 4.32 % with $V_{oc}$ of 0.94 V, a $J_{sc}$ of 8.84 mA/cm$^2$ and FF of 0.52, which is superior to that of PSC based on $\textbf{P2}$:PC$_{71}$BM with $V_{oc}$
of 0.96 V, J_{sc} of 7.26 mA/cm\(^2\) and FF of 0.50. The V_{oc} of both devices is quite high and almost the same which is attributed to the deep and similar values of HOMO energy levels, since the V_{oc} of a BHJ PSC is related to the HOMO of donor and LUMO of acceptor energy offset [30]. The higher PCE of the device based on P1 as compared to P2 under identical conditions is mainly due to the enhanced value of J_{sc} for the former than the later, and all other parameters are slightly changed. The increased J_{sc} could be confirmed from the IPCE spectra (Figure 7b). As shown in Figure 7b, the IPCE response of these devices covers a broad range from 350 to 1100 nm and 350 to 1200 nm for P1:PC\(_{71}\)BM and P2:PC\(_{71}\)BM, respectively, which corresponds to absorption of both copolymer donor and fullerene. Although the IPCE spectrum is broader for P2:PC\(_{71}\)BM than that for P1:PC\(_{71}\)BM, but the IPCE values for former device are higher than that of the later. This means that more excitons are generated into the P2:PC\(_{71}\)BM than P1:PC\(_{71}\)BM, but the exciton dissociation rate in higher for P1:PC\(_{71}\)BM than that for P2:PC\(_{71}\)BM. The exciton dissociation rate depends upon the LUMO offset between the donor and acceptor and should be higher than the exciton binding energy (~0.30 eV). Since the LUMO offset for P2:PC\(_{71}\)BM is around 0.26 eV, and all the excitons generated in this layer are not dissociated into free charge carriers due to insufficient driving force for exciton dissociation and resulted low J_{sc} and IPCE.

The energy loss i.e. E_g-qV_{oc} is the factor also be responsible for the overall PCE of the organic polymer solar cell and this should be greater than 0.5 eV [31, 20b]. In our devices, this loss is about 0.52 eV and 0.44 eV for P1 and P2 based devices, respectively, considering the energy gap is electrochemical bandgap. The higher value for P1 may be responsible higher PCE than P2. These low energy losses may be related to the molecular constitution of conjugated plane.

The overall PCE of the PSC using P1 or P2 as electron donor and PC\(_{71}\)BM as electron acceptor is low compared to the latest development in PSCs. Although the V_{oc} of these devices is quite high, their low PCE is mainly due to the low J_{sc} and FF. These two parameters are directly related to the light harvesting efficiency of the active layer, film morphology, exciton dissociation rate and charge transport. It can be seen from the absorption spectra of P1:PC\(_{71}\)BM and P2:PC\(_{71}\)BM that the absorption covers a broad wavelength region of the solar spectrum and we conclude that the low J_{sc} may be attributed to poor nanoscale morphology of the active layer and charge transport. For an efficient PSC, the BHJ active layer should be composed of a bi-continuous network of donor and acceptor component. In most of the organic BHJ organic solar cells, the J_{sc} value is related to both electron and hole transport efficiencies within the active layer. The electron mobility is
usually quite higher than that of the hole mobility, resulting in unbalanced charge transport [32]. Moreover, well defined nanoscale morphology with better phase separation within exciton diffusion length in the active layer is necessary for efficient exciton dissociation and charge transport [33] and also to minimize the charge pair recombination [34]. It has been reported that solvent vapor annealing (SVA) using polar solvents before deposition of cathode is an effective way to increase the PCE of the PSCs via the formation of more favorable nanomorphology and phase separation [35]. Therefore, we have employed a SVA treatment of the active layers to improve the PCE of PSCs based on these copolymers. It can be seen from Figures 7 and table 4 that compared to the performance of the PSCs without SVA treatments, the PCEs of these copolymers based PSCs increased significantly after the SVA treatment of the active layers. The PCEs increased from 4.32 % to 7.27 % and 3.48 % to 6.41 % for the P1 and P2 based devices, respectively. To our best knowledge, the PCE of 7.27 % is the highest value for ultra low bandgap copolymers with D-A structure. It can be seen from the table 2 that the $V_{oc}$ of these devices with SVA treated active layers is slight lower than that of the counterpart devices based on active layers without SVA, which is also reported earlier [36]. On the other hand, the $J_{sc}$ and FF have been significantly increased leading the higher values of PCEs for the devices with SVA treated active layers. The $J_{sc}$ values improved from 8.84 to 12.62 mA/cm$^2$ and 7.26 to 11.24 mA/cm$^2$ for P1 and P2 devices, respectively. The IPCE spectra were also measured and found that the IPCE values are higher for the devices with SVA treated active layer as compared to that for without SVA treated counter part. The enhancement in $J_{sc}$ and FF for SVA treated devices is also confirmed by measuring the series resistance ($R_s$) and shunt resistance ($R_{sh}$). The observed lower value in $R_s$ and higher value of $R_{sh}$ are essential for high $J_{sc}$ and FF [23]. The lower and higher values of $R_s$ and $R_{sh}$, respectively, indicate better ohmic contact at the interfaces of active layer/cathode or anode, which is beneficial for charge transport and extraction.

Mobilities are an important defining parameter for the performance of the BHJ organic solar cells. Since PCBM has high enough electron transporting ability, the hole mobilities of copolymers are crucial for organic solar cells. Therefore, we have measured the hole mobilities of the copolymers in the active layers using space charge limited current (SCLC) method [37] applied to hole only devices i.e. ITO/PEDOT:PSS/P1 or P2:PC$_{71}$BM/Au (Figure 8). The hole mobility values in active layer were estimated via fitting these curves, in which the current in SCLC region ($J_{sclc}$) is expressed as
where $\varepsilon_o$ and $\varepsilon_r$ are the permittivity of free space and relative dielectric constant of the active layer, $\mu$ is the hole mobility and $L$ is the thickness of the active layer. Without SVA treatments, the hole mobilities are $3.42 \times 10^{-5}$ cm$^2$/Vs and $2.96 \times 10^{-5}$ cm$^2$/Vs for P1 and P2 blended films, respectively. The hole mobility for P1 is slightly higher than that for P2 that supports the high value of $J_{sc}$ for P1 based device. The P1 and P2 blended films with SVA treatments exhibited relatively higher mobilities of $2.45 \times 10^{-4}$ and $1.34 \times 10^{-4}$ cm$^2$/Vs, respectively. The higher hole mobilities of the SVA treated blends could effectively increase the charge carrier transport and thereby resulting in higher $J_{sc}$ values and PCE of the PSCs based on SVA treated active layers.

To obtain further information about the effect of SVA on the charge generation and extraction processes, the variation of photocurrent ($J_{ph}$) with internal voltage of the devices was investigated. The photocurrent ($J_{ph}$) is the difference between the current under illumination ($J_{L}$) and dark current ($J_{D}$), i.e. $J_{ph} = J_{L} - J_{D}$. The $J_{ph}$ can be expressed as $J_{ph} = qLG_{\text{max}}P_c$, where $L$ is the thickness of the active layer, $G_{\text{max}}$ is the maximum generation rate for electron-hole pairs and $P_c$ is the charge collection probability [38-40]. In any solar cell, upon illumination the photoactive layer absorbs solar photons and generates excitons, which undergo dissociation at D/A interfaces, forming bound e-h pairs. The bound e-h pairs are separated into free charge carriers and then drifted toward different electrodes under the drive of internal field. The internal effective field is defined as $V_{\text{eff}} = V_o - V_{\text{appl}}$, where $V_o$ is the voltage at which $J_{ph}$ is zero and $V_{\text{appl}}$ is the applied voltage. The variation of $J_{ph}$ with internal voltage $V_{\text{eff}}$ is shown in Figure 9. The log-log plot of $J_{ph}$ versus $V_{\text{int}}$ shows two distinct regions: a linear region and a saturation region, where $J_{ph}$ was saturated at $V_o - V_{\text{appl}} > 0.52$ V for devices based on SVA treated active layers. The field independent saturation region suggests negligible trapped charges and efficient charge extraction and collection. On the other hand, the devices based on the active layers without SVA treatment showed no clear saturation in $J_{ph}$ with increasing $V_{\text{int}}$, indicating significant electron-hole recombination, where a stronger internal electric field is needed to sweep out the photogenerated charge carriers and separate the germinate electron-hole pairs [41]. This is closely related to the film morphology of active layer with SVA, which hinders efficient charge transport. In addition, the photogenerated $J_{ph}$ of SVA treated devices were higher than that of devices without SVA, suggesting higher charge generation and charge extraction. The values of $G_{\text{max}}$ can be...
calculated by \( J_{\text{phsat}} = q G_{\text{max}} L \). The increase in the value of \( G_{\text{max}} \) for SVA treated devices suggests that the treatment of SVA amplifies the exciton generation rate, which is a measure of the number of photons absorbed [42, 43]. These results are consistent with the absorption profile and morphology of active layers and photovoltaic performance of the devices. To obtain information about the exciton dissociation efficiency and charge collection efficiency, the ratio of \( J_{\text{sc}} \) to \( J_{\text{phsat}} \) was estimated [44] to be 0.69, 0.64, 0.86 and 0.82 for \( \text{P1:PC}_{71}\text{BM} \) (as cast), \( \text{P2:PC}_{71}\text{BM} \) (as cast) \( \text{P1:PC}_{71}\text{BM} \) (SVA) and \( \text{P2:PC}_{71}\text{BM} \) (SVA) active layers. The larger values of this ratio for the devices processed with SVA treatment are attributed to better phase separation in the active layer, increased hole mobility, improved balanced charge transport and enhancement in the light harvesting ability. All these parameters demonstrate that SVA improves the exciton dissociation efficiency, and charge transport and collection efficiency, and also reduces the carrier recombination.

Nanoscale phase separation within the blended active layer is required for high performance PSCs. It provides not only a large interfacial area for exciton dissociation but also continuous percolating path for electron and hole transport to the corresponding electrodes [45]. Transmission electron microscopy (TEM) is an important tool to get information about the morphology of the active layers. In order to get information about the effect of SVA treatment on the morphology of active layers, we have recorded the TEM images of these active layers and are shown in Figure 10. The black domain is assigned to \( \text{PC}_{71}\text{BM} \) aggregation because its ordered aggregation gives relatively higher electron density compared to polymer aggregation [46]. The as cast active layer showed a finer network of bright and dark region with slight phase separation between copolymer and \( \text{PC}_{71}\text{BM} \) phase. The size of bright and dark regions of the blended film with SVA treatment is increased indicating more appropriate nanophase separation, which is beneficial for exciton dissociation and charge transport. Therefore the better phase separation induced by SVA leads to increased \( J_{\text{sc}} \) and FF leading an enhancement in the overall PCE of the PSCs.

Conclusions

We designed two ultra low bandgap D-A copolymers with same thiadiazoloquinoxaline unit as the main electron accepting unit (A) and different benzodithiophene (BDT) and dithienosilole (DTS) as donor unit (D) units and their optical and electrochemical properties were compared. These copolymers were used as donor material for solution processed bulk heterojunction polymer solar cells. After the optimization of active layers, i.e. weight ratio and solvent vapor treatment, PSC based on \( \text{P1:PC}_{71}\text{BM} \) blend showed higher PCE (7.27 %) as compared that for \( \text{P2:PC}_{71}\text{BM} \) (6.68 %).
The higher PCE is mainly attributed to improvement in Jsc and FF. Although the P2 showed border absorption profile than P1, the lower Jsc is mainly attributed to the low driving force for exciton dissociation arises from the LUMO off set ~0.26 eV. The increase in PCE with SVA treatment of active layer may be attributed to the favorable nanoscale morphology and higher hole mobility.

Acknowledgements

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References


27. TURBOMOLE (version 5.6); Universitat Karlsruhe, 2000.


Table 1 Molecular weight and thermal properties and yield of P1 and P2 copolymers.

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>Yield (%)</th>
<th>(M_n) (kg/mol)</th>
<th>(M_w) (kg/mol)</th>
<th>PD</th>
<th>(T_d)(^a) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>81</td>
<td>10.4</td>
<td>20.2</td>
<td>1.94</td>
<td>335</td>
</tr>
<tr>
<td>P2</td>
<td>66</td>
<td>8.3</td>
<td>13.0</td>
<td>1.57</td>
<td>408</td>
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</table>

\(^a\)\(T_d\) is the 5% weight-loss temperature of polymer under inert atmosphere.

Table 2 Optical and electrochemical data of P1 and P2 copolymers

<table>
<thead>
<tr>
<th>Copolymer</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(\lambda_{\text{max}}) (nm)</th>
<th>(E_g^{\text{opt}}) (eV)</th>
<th>(E_{\text{onset}}^{\text{red}}) (V)</th>
<th>(E_{\text{onset}}^{\text{red}}) (V)</th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>(E_{\text{opt}}^{\text{elec}}) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>332, 429, 886</td>
<td>345, 439, 952</td>
<td>1.16</td>
<td>0.94</td>
<td>-0.52</td>
<td>-5.34</td>
<td>-3.88</td>
<td>1.46</td>
</tr>
<tr>
<td>P2</td>
<td>358, 432, 964</td>
<td>358, 439, 1022</td>
<td>1.08</td>
<td>0.94</td>
<td>-0.46</td>
<td>-5.34</td>
<td>-3.94</td>
<td>1.40</td>
</tr>
</tbody>
</table>

Table 3 Calculated properties of P1 and P2. Specifically HOMO and LUMO energies (eV), HOMO–LUMO gap (eV), \(\lambda_{1\text{st/max}}\) (nm), \(f\), the main contributions to the first excited state, and the dipole moment (D), \(\mu\).

<table>
<thead>
<tr>
<th></th>
<th>HOMO (eV)</th>
<th>LUMO (eV)</th>
<th>HL (eV)</th>
<th>OG (eV)</th>
<th>(\lambda_{1\text{st/max}}) (nm)</th>
<th>(f)</th>
<th>Main Contributions</th>
<th>(\mu) (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB44</td>
<td>-4.25</td>
<td>-3.46</td>
<td>0.79</td>
<td>1.12</td>
<td>1109</td>
<td>0.21</td>
<td>H→L (83%), H→L (17%)</td>
<td>2.31</td>
</tr>
<tr>
<td>PBE</td>
<td>-4.44(^a)</td>
<td>-3.63(^a)</td>
<td>0.82(^a)</td>
<td>1.08(^a)</td>
<td>1146(^a)</td>
<td>0.26(^a)</td>
<td>H→L (82%), H→L (18%)(^a)</td>
<td>3.38(^a)</td>
</tr>
<tr>
<td>B3LYP</td>
<td>-4.83</td>
<td>-3.04</td>
<td>1.79</td>
<td>1.52</td>
<td>817/453/381/337/334/323</td>
<td>0.29</td>
<td>H→L (100%)</td>
<td>2.77</td>
</tr>
<tr>
<td>P</td>
<td>-5.03(^a)</td>
<td>-3.19(^a)</td>
<td>1.84(^a)</td>
<td>1.51(^a)</td>
<td>822/451/386/338/331/324(^a)</td>
<td>0.35(^a)</td>
<td>H→L (100%)(^a)</td>
<td>3.65(^a)</td>
</tr>
<tr>
<td>M06</td>
<td>-5.11</td>
<td>-2.97</td>
<td>2.14</td>
<td>1.59</td>
<td>780/437/414/323/314</td>
<td>0.29</td>
<td>H→L (100%)</td>
<td>2.80</td>
</tr>
<tr>
<td></td>
<td>-5.32(^a)</td>
<td>-3.14(^a)</td>
<td>2.18(^a)</td>
<td>1.57(^a)</td>
<td>788/434/323/315/283(^a)</td>
<td>0.35(^a)</td>
<td>H→L (99%)(^a)</td>
<td>3.88(^a)</td>
</tr>
</tbody>
</table>

|          | PBE      | -4.17     | -3.39   | 0.78    | 1.15    | 1080 | 0.26   | H→L (98%)        | 2.37        |

\(^a\)SB50
Table 4 Photovoltaic parameters of organic BHJ solar cells based on optimized P1:PC$_{71}$BM and P2:PC$_{71}$BM active layers

<table>
<thead>
<tr>
<th>Active layer</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>$V_{oc}$ (V)</th>
<th>FF</th>
<th>PCE (%)</th>
<th>$R_s$ (Ω cm$^2$)</th>
<th>$R_{sh}$ (Ω cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1:PC$_{71}$BM (as cast)</td>
<td>8.84</td>
<td>0.94</td>
<td>0.52</td>
<td>4.32</td>
<td>34</td>
<td>409</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM (as cast)</td>
<td>7.26</td>
<td>0.96</td>
<td>0.50</td>
<td>3.48</td>
<td>56</td>
<td>308</td>
</tr>
<tr>
<td>P1:PC$_{71}$BM (SVA)</td>
<td>12.62</td>
<td>0.90</td>
<td>0.64</td>
<td>7.27</td>
<td>18</td>
<td>676</td>
</tr>
<tr>
<td>P2:PC$_{71}$BM (SVA)</td>
<td>11.72</td>
<td>0.92</td>
<td>0.62</td>
<td>6.68</td>
<td>23</td>
<td>649</td>
</tr>
</tbody>
</table>

Values when solvent effects are taken into account for chloroform.

Scheme 1 Stille coupling synthesis of P1 and P2 D-A copolymers.
Figure $^{1}$$HNMR$ spectra of copolymers (a) P1 and (b) P2 in CDCl$_3$
Figure 2 TGA curves copolymers with a heating rate of 10°C min⁻¹ under an inert atmosphere.

Figure 3 Normalized absorption spectra of (a) P1 and (b) P2 in dilute chloroform solution and in thin film cast from chloroform solution.
Figure 4 Cyclic voltammograms of the copolymers P1 and P2 films cast on platinum electrode in 0.1 mol/L Bu₄NOCl/CH₃CN at scan rate 50 mVs⁻¹
Figure 5 Frontier orbitals i.e. HOMO and LUMOs of (top) P1, and (bottom) P2.

Figure 6 Theoretical UV/Vis absorption spectrum of (a) P1, and (b) P2 (calculated using the M06 functional).
Figure 7 (a) Current–voltage (J-V) characteristics under illumination and (b) IPCE spectra of the devices based on optimized P1:PC$_{71}$BM and P2:PC$_{71}$BM active processed under different conditions.
Figure 8 J–V curves of the hole only devices based on optimized P$_1$:PC$_{71}$BM and P$_2$:PC$_{71}$BM active processed under different conditions.

Figure 9 Variation of photocurrent density ($J_{ph}$) with the effective internal voltage ($V_{eff}$) for the devices based on based on P$_1$:PC$_{71}$BM and P$_2$:PC$_{71}$BM active layers processed as cast and SVA treatment.
Figure 10 TEM images of P1:PC$_{71}$BM with scan bar 200 nm.