Synthesis and Photovoltaic Properties of Two-Dimensional Low-Bandgap **Copolymers Based on New Benzothiadiazole Derivatives with Different Conjugated Aryl-vinylene Side Chains**

Qiang Peng,*^[a, c] Siew-Lay Lim,^[b] Ivy Hoi-Ka Wong,^[b] Jun Xu,^[c] and Zhi-Kuan Chen*^[b]

Abstract: A new series of 2,1,3-benzothiadiazole (BT) acceptors with different conjugated aryl-vinylene side chains have been designed and used to build efficient low-bandgap (LBG) photovoltaic copolymers. Based on benzo[1,2-b:3,4-b']dithiophene and the resulting new BT derivatives, three two-dimensional (2D)-like donor (D)acceptor (A) conjugated copolymers have been synthesised by Stille coupling polymerisation. These copolymers were characterised by NMR spectroscopy, gel-permeation chromatography, thermogravimetric analysis and differential scanning calorimetry. UV/Vis absorption and cyclic voltammetry measurements indicated that their optical and electrochemical properties can be

Introduction

Harvesting energy directly from the sun is one of the most efficient approaches to address the growing global energy needs. Recently, polymer solar cells (PSCs) have received increasing attention because of their flexibility, facile processibility, light weight and low production cost.^[1] Considerable effort has been focused on improving the power conversion efficiency (PCE) of PSCs from around 1 to 9% for potential commercial applications.^[2] In earlier times, high PCEs of 4-5% were achieved by blending P3HT as a donor and [6,6] phenyl-C61-butyric acid methyl ester (PC₆₁BM) as an

[a] Prof. Q. Peng College of Chemistry, Sichuan University Chengdu, 610064 (P. R. China)

[b] Dr. S.-L. Lim, Dr. I. H.-K. Wong, Prof. Z.-K. Chen Institute of Materials Research and Engineering 3 Research Link, Singapore, 117602 (Singapore) Fax: (+86)28-86510868 E-mail: qiangpengjohnny@yahoo.com zk-chen@imre.a-star.edu.sg

[c] Prof. Q. Peng, M. Sc. J. Xu School of Environmental and Chemical Engineering Nanchang Hangkong University Nanchang, 330063 (P. R. China)

facilely modified by changing the structures of the conjugated aryl-vinylene side chains. The copolymer with phenyl-vinylene side chains exhibited the best light harvesting and smallest bandgap of the three copolymers. The basic electronic structures of D-A model compounds of these copolymers were also studied by DFT calculations at the B3LYP/6-31G* level of theory. Polymer solar cells (PSCs) with a typical structure of indium tin oxide (ITO)/ poly(3,4-ethylenedioxythiophene) (PE-DOT):poly(styrenesulfonate) (PSS)/

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copolymer:[6,6]-phenyl-C₆₁(C₇₁)-butyric acid-methyl ester (PCBM)/calcium (Ca)/aluminum (Al) were fabricated and measured under the illumination of AM1.5G at 100 mW cm^{-2} . The results showed that the device based on the copolymer with phenyl-vinylene side chains had the highest efficiency of 2.17% with PC71BM as acceptor. The results presented herein indicate that all the prepared copolymers are promising candidates for roll-to-roll manufacturing of efficient PSCs. Suitable electronic, optical and photovoltaic properties of BT-based copolymers can also be achieved by fine-tuning the structures of the aryl-vinylene side chains for photovoltaic application.

acceptor by using the typical bulk-heterojunction (BHJ) device structure.^[3] However, the mismatch between the absorption of the devices and the terrestrial solar spectrum limited their performance in PSCs. To achieve enhanced absorption, low-bandgap (LBG) conjugated polymers were developed by incorporating electron-rich donor (D) and electron-deficient acceptor (A) segments into the polymer backbones.^[4,5] The push-pull interaction of the donor and acceptor moieties can result in a lower-energy absorption band due to intramolecular charge transfer (ICT).^[6] Based on this concept, PCEs of over 7% were obtained by using LBG conjugated copolymers in bulk-heterojunction (BHJ) solar cells as electron-donating materials.^[7]

To date, most LBG copolymers have linear main-chain structures. In the past few years, two-dimensional (2D)-like copolymers with conjugated side chains were proposed to enhance absorption, charge transport and device performance.^[4a,8] Li and co-workers designed and prepared a series of polythiophenes with conjugated side chains of bi(phenylenevinylene),^[8a] bi(thienylenevinylene)^[8b,c] and phenothiazinevinylene,[8d] which exhibited broadened absorption spectra and enhanced power conversion efficiencies. Other interesting work with 2D-like polythiophenes in PSCs included the use of conjugated side chains of triphenylamine,^[9a] carbazole,^[9b] phenothiazine^[9c] and phenanthrenylimidazole.^[9d,e] Very

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recently, Huang et al. reported a novel 2D D–A conjugated copolymer system in which the strong electron-withdrawing acceptor groups were attached to the end of the side chains connecting the electron-donating conjugated main chain through a bridge.^[10] By this method, low bandgaps can be effectively obtained and relatively low highest-occupied molecular orbital (HOMO) energy levels can be easily maintained.^[11] The BHJ solar cells based on these copolymers exhibit high PCE values of over 4%.^[10,11] Although previous work has proved that 2D-like conjugated copolymers are promising candidates for building efficient LBG photovoltaic copolymers, it still remains a challenge to develop new systems and understand the relationship between their structures and properties.

In this work we have designed and synthesised a series of 2D-like D-A conjugated copolymers, **PBDBT1**, **PBDBT2** and **PBDBT3** (Figure 1), with novel 2,1,3-benzothiadiazole



Figure 1. Structures of the LBG copolymers **PBDBT1**, **PBDBT2** and **PBDBT3**.

(BT) acceptors modified with conjugated aryl-vinylene side chains for efficient BHJ solar cell application. The parent skeleton of the BT acceptor was chosen because it has been widely employed and proven to be one of the most promising acceptor blocks for building high-performance polymer solar cell materials.^[12] In fact, LBG copolymers containing BT and various donor segments, such as fluorene,^[13] silafluorene,^[14] carbazole,^[15] indolo[3,2-b]carbazole,^[16] dithienosilole,^[17] dithieno[3,2-*b*:2',3'-*d*]pyrrole,^[18] benzo[1,2-*b*:4,5b']dithiophene,^[19] showed high PCEs ranging from 2 to 7%. Clearly, almost all the work was focused on naked BT or alkyl- and alkoxy-modified BT frameworks, but not all of the important properties of the BT unit and its derivatives have been explored fully. Thus, it is reasonable to expect that the prepared copolymers would have good photovoltaic properties. The effects of different conjugated aryl-vinylene side chains, donor-acceptor strength and backbone planarity on the absorption spectra and electronic and optoelectronic properties of the resulting copolymers have also been investigated. To our knowledge, this is the first report of the use of 2D-like benzothiadiazole units as acceptors with conjugated side chains for the construction of efficient LBG copolymers for PSC application.

Results and Discussion

Synthesis and characterisation: The synthetic routes to the monomers and copolymers are outlined in Scheme 1. 4,7-Dibromo-5-methyl-2,1,3-benzothiadiazole (3) was prepared by bromination of 5-methyl-2,1,3-benzothiadiazole with Br₂ and HBr (47%) according to the procedure used for the synthesis of 4,7-dibromo-2,1,3-benzothiadiazole.^[16c] 4,7-Dibromo-5bromomethyl-2,1,3-benzothiadiazole (4) was synthesised from compound 3 by further bromination with NBS by using benzoyl peroxide (BPO) as the radical initiator. Benzothiadiazole 4 was subsequently treated with triethyl phosphite to give phosphonic acid diethyl ester 5. 2D-Like benzothiadiazole derivatives 6a-c were synthesised by the Wittig-Horner reaction by coupling 5 with various aromatic aldehydes, which then underwent the further coupling reactions and brominations to monomer 8a-c. The copolymers were synthesised in good yields from organic tin compounds and bromides 8 by Stille coupling reactions with $[Pd_2(dba)_3]/$ $P(o-tolyl)_3$ as catalyst. The crude copolymers **PBDBT1**-PBDBT3 were purified by washing with methanol and hexane in turn and then extraction with chloroform, respectively. The chloroform solution was concentrated and reprecipitated in methanol several times to give the resulting copolymer. The structures of the copolymers were confirmed by NMR spectroscopy.

Owing to presence of the attached dodecyl and dodecyloxy side chains, these copolymers exhibit good solubility in organic solvents such as chloroform, tetrahydrofuran, toluene, xylene and chlorobenzene. The number-average molecular masses (M_n) and polydispersity indices (PDI) were measured by gel-permeation chromatography (GPC) using THF as the eluent and polystyrenes as the internal standards. The results show that **PBDBT1–PBDBT3** have high number average molecular mass values ranging from 39200 to 66100 Da with the PDI values ranging from 2.08 to 2.57 (Table 1). The glass transition temperatures (T_g) of these co-

Table 1. Molecular weights and thermal properties of the copolymers.

Copolymers	Yield [%]	$M_{ m n}^{[m a]}$	PDI ^[a,b]	$T_{\rm d}^{\rm [c]} \left[{}^{\mathbf{o}} \mathrm{C} \right]$	$T_{\rm g}^{\rm [d]}\left[^{\rm o}{\rm C} ight]$
PBDBT1	73	39200	2.08	339	119
PBDBT2	80	66100	2.57	333	99
PBDBT3	91	52400	2.21	345	106

[a] Molecular masses and polydispersity indices were determined by GPC in THF with polystyrene as standards. [b] The PDI is defined as M_w/M_n . [c] Onset decomposition temperature measured by TGA under N₂. [d] Glass transition temperature measured by DSC under N₂.

polymers (Figure 2a) were determined to be in the range 99–119 °C by differential scanning calorimetry (DSC). The copolymers exhibit good thermal stability with decomposition onset temperatures (T_d ; about 5% weight loss) of 333–345 °C, as measured by thermogravimetric analysis (TGA; Figure 2b). Clearly, the combination of such good thermal properties renders these copolymers suitable for application in PSCs, light-emitting diodes and other optoelectronic devices.

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Scheme 1. Synthetic routes to the monomers and conjugated copolymers.

Optical properties: The electronic absorption properties of the copolymers obtained were measured both in CHCl₃ solution (Figure 3a) and as thin films spin-coated on to quartz slides (Figure 3b). The spectroscopic data are listed in Table 2. As shown in Figure 3a, the absorption spectra of these copolymers in CHCl₃ present two absorption bands, as is commonly observed in conjugated D-A copolymers.^[5] The broad distinct peak in the wavelength range 450-800 nm arises from intramolecular charge-transfer transitions (ICT) between the donor segments and the acceptor moieties.^[20] Another peak ranging from 350 to 450 nm can be attributed to the π - π * electronic transitions of the conjugated polymer backbones. PBDBT1, PBDBT2 and PBDBT3 have absorption maxima at 402 and 562, 393 and 539, and 410 and 579 nm, respectively. Relative to PBDBT1 and PBDBT2, the absorption maxima of PBDBT3 show slight redshifts, which can be attributed to the higher formed ICT from the donor to the acceptor. It is surprising that **PBDBT2** with an electron-withdrawing carbonyl group

Table 2. Optical and electrochemical data of the copolymers.

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Copolymers	Absor $\lambda_{\max}^{\text{THF}}$ [nm]	rption $\lambda_{\max}^{\text{film}}$ [nm]	$E_{\rm g}^{[a]}$ [eV]	$\frac{E_{\text{onset}}^{\text{ox}} [\text{V}]}{\text{HOMO}}$ [eV]	E ^{red} _{onset} [V]/ LUMO [eV]	$E_{\mathrm{g}}^{\mathrm{[b]}}$ [eV]
PBDBT1	402,	417,	1.67	0.75/-5.15	-0.78/-3.62	1.54
PBDBT2	562 393, 539	603 413, 598	1.71	0.87/-5.27	-0.75/-3.65	1.62
PBDBT3	410, 579	420, 606	1.66	0.68/-5.08	-0.83/-3.57	1.51

[a] The optical band gap was estimated from the wavelength of the optical absorption edge of the copolymer film. [b] The electrochemical band gap was calculated from the LUMO and HOMO energy levels.

in the dodecanoylthienyl-vinylene side chain has the most blue-shifted absorbance spectrum. The results also indicate that the conjugated side chains can easily tune the absorption behaviour of BT-based D-A copolymers, which is very useful for the design and preparation of efficient photovolta-

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Figure 2. a) DSC and b) TGA curves of the copolymers (recorded under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹).



Figure 3. Optical absorption spectra of the copolymers a) in CHCl₃ solution and b) as thin film on glass.

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ic materials with enhanced absorption and suitable energy levels. When the polymer solutions were heated to 80°C, the absorption peaks were slightly blueshifted (Figure 3a), which indicates the partial disaggregation of the polymer backbone at high temperature.

As shown in Figure 3b, similar behaviour was observed from the absorption spectra of these copolymers as solid thin films. Relative to their counterparts in the solution state, the broad peaks in the wavelength range of 450-900 nm are redshifted by 41, 59 and 27 nm for PBDBT1, PBDBT2 and PBDBT3, respectively. This can be explained by the formation of π -stacked structures in the solid state,^[21] which could facilitate charge transportation for photovoltaic applications. Although PBDBT2 has a narrow absorption band, it presents the best π -stacked structures with the longest redshifted maxima. This may be because the carbonyl group increases the interaction between the polymer main chains. The energy band gaps calculated from the absorption band edges of the optical absorption spectra are around 1.67, 1.71 and 1.66 eV for PBDBT1, PBDBT2 and PBDBT3, respectively. This indicates that PBDBT3 with weaker electron-donating phenyl-vinylene side chains shows a stronger ICT effect than PBDBT1 and PBDBT2, leading to a smaller bandgap, which is useful for increasing the short circuit current (J_{sc}) in PSCs.^[3a,22] As expected, the optical bandgaps and broad absorption bands across the entire visible wavelength region of the BT-based copolymers can be fine-tuned by modifying the structures of the conjugated side chains, which suggests that this strategy can be employed to develop efficient photovoltaic materials with improved properties.

Electrochemical properties: Cyclic voltammetry (CV) was employed to determine the highest-occupied (HOMO) and lowest-unoccupied molecular orbital (LUMO) energy levels of the polymeric materials. These energy levels are crucial for the selection of appropriate acceptor materials in active blends in PSCs. The CV experiments were carried out by using a three-electrode cell in an anhydrous CH₃CN solution of 0.1 M tetrabutylammonium perchlorate (*n*Bu₄NClO₄). A platinum plate coated with a thin film of the studied copolymer, a platinum wire and Ag/AgCl (0.1 M) were used as the work, counter and reference electrodes, respectively. The energy level of the Ag/AgCl reference electrode was calibrated against the Fc/Fc+ system to be 4.40 eV by using previous methods.^[23] The resulting oxidation and reduction curves of the copolymer thin films are shown in Figure 4 and the electrochemical redox data are summarised in Table 2. The cell was purged with pure argon prior to each scan. The scans in the anodic and cathodic directions were performed separately at a scan rate of 50 mVs⁻¹ at room temperature. As shown in Figure 4, all the copolymers show a predominant oxidation peak (p doping) due to the electron-donating benzodithiophene, thiophene and aryl-vinylene segments and a slight reduction peak (n doping) related to the electron-withdrawing benzothiadiazole unit. From the onset potentials of the p-doping process, the HOMO energy



Figure 4. Cyclic voltammograms of the copolymers.

levels were determined to be -5.15, -5.27 and -5.08 eV for **PBDBT1**, **PBDBT2** and **PBDBT3**, respectively. These results indicate that carbonylthienyl-vinylene can lower the HOMO level in this polymer system compared with thienyl-vinylene and phenyl-vinylene, which is expected to increase the open-circuit voltage (V_{oc}) of the PSCs.^[2d] On the other hand, the LUMO energy levels were estimated to be -3.62, -3.65 and -3.57 eV for **PBDBT1**, **PBDBT2** and **PBDBT3** from the onset potentials of the cathodic sweep, respectively. Thus, the band gaps (E_g) of **PBDBT1**, **PBDBT2** and **PBDBT3** were calculated to be around 1.54, 1.62 and 1.51 eV. The values and their trends are consistent with those obtained by the optical method described above.

Theoretical calculations: DFT/B3LYP/6-31G* has been found to be an accurate method for calculating the optimal geometries and electronic structures of many molecular systems. To better understand the evolution of the oxidation and reduction potentials, the electronic structures of the conjugated copolymers, molecular simulation on D-A model compounds was performed through DFT calculations^[24] at the B3LYP/6-31G* level of theory by using the Gaussian 09 program suite.^[25] To make computation possible, the alkyl groups were replaced by methyl groups in the calculations because they do not significantly affect the equilibrium geometries or electronic properties. The frontier molecular orbitals and optimised molecular geometries are illustrated in Figure 5. Ab initio calculations on the model compounds indicate that they favour planar conformations, which enables the electrons to be delocalised across the whole conjugated molecular system for higher carrier mobility.^[26] As shown in Figure 5, the electron density of the LUMO is mainly localised on the benzothiadiazole segment for BD-BT1 and BD-BT3. Owing to the electron-withdrawing nature of the carbonyl group, the LUMO of BD-BT2 is delocalised over the conjugated section from the benzothiadiazole to the carbonyl group through the thienyl-vinylene linker. At the same time, as a result of the carbonyl group, the electron density of the HOMO of BD-BT2 is distributed over the entire conjugated molecule including the conjugated side chain, which lowers the HOMO energy level giving rise to the enhanced V_{oc} in PSCs. The calculations show that the D–A model molecules have HOMO and LUMO energy levels in the range of -5.02 to -5.15 eV and -2.55 to -2.63 eV, respectively. The band gaps were thus determined to range from 2.47 to 2.52 eV. Clearly, the trends in the HOMOs, LUMOs and band gaps are similar to those obtained by CV and UV/Vis measurements of the copolymers. Although the calculated values are somewhat different from the experimental data because of the part-extended π -conjugation system or because only several repeating sections were selected from the copolymers, the theoretical analysis of the geometric structures and electronic structures is still important to gain a direct insight into the interplay between their structural modifications and the resulting electronic and optical changes.

Photovoltaic properties: To verify the potential of the copolymers for photovoltaic application, bulk heterojunction solar cells were fabricated and investigated according to our previous work^[2d,5d,20] with a conventional configuration of glass/indium tin oxide (ITO)/poly(3,4-ethylenedioxythiophene) (PEDOT):poly(styrenesulfonate) (PSS)/copolymer:-[6,6]-phenyl-C₆₁(C₇₁)-butyric acid-methyl ester (PCBM)/calcium (Ca)/aluminum (Al). The devices were optimised by changing some conditions, such as the ratio of the copolymer to PCBM and the thickness of the active layer. The active layers were spin-coated from 1,2-dichlorobenzene (DCB) solutions of the copolymers and PCBM, and the optimal weight ratio of copolymer to PC₆₁BM was found to be 1:1 for PBDBT1, PBDBT2 and PBDBT3. The optimal thicknesses for blend films of PBDBT1, PBDBT2 and PBDBT3 with PCBM were about 110, 85 and 75 nm, respectively. The representative characteristics of the solar cells are summarised in Table 3. Note that the device based on PBDBT3 with phenyl-vinylene side chain exhibits much better photovoltaic performance than those made from PBDBT1 and PBDBT2 with thienyl-vinylene side chains.

Figure 6 shows the current density-voltage (J-V) curves and external quantum efficiency (EQE) spectra for the PSCs under AM1.5G illumination at 100 mW cm⁻². As shown in Figure 6a, the **PBDBT1** and **PBDBT2** devices

Table 3. Characteristic current density-voltage parameters derived from devices tested under standard AM1.5G conditions.

Copolymer	Copolymer/PCBM (w/w)	$V_{\rm oc}$ [V]	$J_{\rm SC}$ [mA cm ⁻²]	FF	PCE [%]
PBDBT1	1:1 ^[a]	0.69	4.82	0.38	1.27
PBDBT1	1:2 ^[a]	0.66	3.97	0.36	0.94
PBDBT1	1:4 ^[a]	0.69	3.98	0.41	1.11
PBDBT1	1:1 ^[b]	0.71	5.51	0.35	1.38
PBDBT2	$1:1^{[a]}$	0.84	3.49	0.35	1.03
PBDBT2	1:2 ^[a]	0.83	2.60	0.39	0.84
PBDBT2	1:4 ^[a]	0.75	1.67	0.40	0.50
PBDBT2	1:1 ^[b]	0.84	3.98	0.38	1.26
PBDBT3	1:1 ^[a]	0.66	5.37	0.54	1.92
PBDBT3	1:2 ^[a]	0.62	4.66	0.42	1.19
PBDBT3	1:4 ^[a]	0.61	4.41	0.44	1.18
PBDBT3	1:1 ^[b]	0.66	6.61	0.50	2.17

[a] Using PC₆₁BM as acceptor. [b] Using PC₇₁BM as acceptor.

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Figure 5. Optimised geometries and molecular orbital surfaces of the HOMOs and LUMOs of the model compounds obtained by DFT at the B3LYP/6-31G* level of theory.

show open-circuit voltages (V_{oc}) of 0.69 and 0.84 V and short-circuit current densities (J_{sc}) of 4.82 and 3.49 mA cm⁻², (The V_{oc} and J_{sc} values can be read from the J-V curves, and the PCE and FF can be calculated from V_{oc} and J_{sc} values from the equations of PCE = $V_{oc}J_{sc}FF/P_{max}$ and FF = $V_{max}J_{max}/V_{oc}J_{sc}$. Here, P_{max} is a fixed value and $V_{max}J_{max}$ can also be calculated from the J-V curves.), which results in PCEs of 1.27 and 1.03% with fill factors (FF) of 0.38 and 0.35, respectively. Under the same conditions, the **PBDBT3** device exhibits a higher PCE of 1.92% with a V_{oc} of 0.66 V, a J_{sc} of 5.37 mA cm⁻² and a FF of 0.54. Of the fabricated devices, the **PBDBT2** device has the highest V_{oc} due to its lowest HOMO energy level, as described previously. Such results are expected as the V_{oc} is dependent on the difference between the HOMO energy level of the donor and the LUMO energy level of the acceptor.^[27] However, the lowest J_{sc} of the **PBDBT2** device results in the lowest PCE, which may be attributed to the larger bandgap of 1.71 eV compared with those of **PBDBT1** and **PBDBT3**. Furthermore, the dodecanoyl unit with a carbonyl group may act as an electron trap compared with the dodecyl and dodecyloxy units. The PCEs were achieved without any pre- and/or post-treatments, such as thermal annealing, solvent/vapour annealing or the addition of solvent additives. Thus, considering the relatively low FF values of 0.35–0.54, there is big room for future improvement in the performance of PSCs based on the copolymer/PCBM system.



Figure 6. a) Current density-voltage curves of photovoltaic cells based on copolymers and PC61BM under AM1.5 illumination and b) EQE curves of photovoltaic cells based on copolymers and PC61BM.

To evaluate the accuracy of the measurements, the EQEs of the PSCs based on the copolymers blended with PC₆₁BM (1:1) under monochromatic illumination were measured and are shown in Figure 6b. The shapes of the EQE curves of the devices based on copolymer:PC61BM are similar to their absorption spectra, which indicates that most of the absorbed photons of the copolymers contribute to the photocurrent generation. That is, the excitons are mainly generated in copolymer phases. As shown in Figure 6b, the spectral responses of the three copolymer:PC61BM based devices exhibit an efficient photoresponse at wavelengths between 300 and 800 nm with maximum EQEs of 42, 30 and 22% at around 500 nm. Meanwhile, the J_{sc} values calculated from the EQEs show a consistent trend with the measured values. Clearly, the broader profile and higher EQE value of **PBDBT3** result in a higher J_{sc} for the **PBDBT3** device compared with the PBDBT1 and PBDBT2 devices.

AFM is one of the key factors in determining the performance of polymer solar cells.^[3b,28] An ideal domain size of 10-20 nm of copolymer and PCBM with an interpenetrating bicontinuous network has been found to be important for achieving high-performance devices. However, both larger (>10-20 nm) and smaller (<10-20 nm) domain sizes of the blend films will limit charge transfer and separation. Figure 7 shows the atomic force microscopy (AFM) topographic images of the films of copolymer: $PC_{61}BM$ (1:1, w/w) blends recorded in tapping mode. All the films exhibit typical cluster structures with many aggregated domains, and



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Figure 7. AFM topographic images of the blend films (copolymer:PC60BM, 1:1, w/w) of a) PBDBT1, b) PBDBT2 and c) PBDBT3. Image size: 2×2 um².

root-mean-square (RMS) roughnesses of 1.80, 1.55 and 2.07 nm were obtained for **PBDBT1**, **PBDBT2** and PBDBT3. respectively. The larger of roughness PBDBT3:PC₆₁BM compared with the PBDBT1 and **PBDBT2** blend films shows the higher degree of ordered structure, which indicates reduced internal series resistance and more efficient charge separation in the PSCs. The film surface with higher roughness and nanoscaled texture also benefits the internal light scattering and enhances light absorption.^[29] All this results in the higher J_{sc} value and efficiency of the PBDBT3 device relative to the PBDBT1 and PBDBT2 devices. Further detailed investigations on the charge transfer and exciton separation and recombination are in progress and will be reported elsewhere.

PC71BM has a similar electronic structure to PC61BM, but a considerably stronger absorption in the visible region.^[30] Thus, the copolymer-based PSCs can be expected to exhibit improved performance when PC71BM is used in place of PC₆₁BM as the acceptor because of the compensation for the poor absorption of the copolymer:PC61BM blend in the 400-500 nm range. To understand the effect of PC71BM on the photovoltaic properties, PSCs with different copolymer:PC₇₁BM ratios were fabricated and investigated. The optimal ratio was found to be 1:1 for all the PC₇₁BM-based devices. The J-V and EQE curves of the PSCs are plotted in Figure 8, and the photovoltaic parameters of J_{sc} , V_{oc} , FF and

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Figure 8. a) Current density-voltage curves of photovoltaic cells based on copolymers and PC71BM under AM1.5 illumination and b) EQE curves of photovoltaic cells based on copolymers and PC71BM.

PCE are summarised in Table 3. As shown in Figure 8a, all of the copolymer devices exhibit some improvement in the PCEs, by 7.8-22%, compared with the corresponding PC₆₁BM-based devices. The **PBDBT1** and **PBDBT2** devices show $V_{\rm oc}$ values of 0.71 and 0.84 V, $J_{\rm sc}$ values of 5.51 and 3.98 mA cm^{-2} , and FFs of 0.35 and 0.38, which results in PCEs of 1.38 and 1.26%, respectively. The PBDBT3 device still shows the highest PCE of 2.17 % with a $V_{\rm oc}$ of 0.66 V, a $J_{\rm sc}$ of 6.61 mA cm⁻² and a FF of 0.50. Figure 8b shows that the poor absorption in the range of 400-500 nm is efficiently compensated. Clearly, the increased absorption enhances light harvesting when PC71BM is used instead of PC61BM, which results in further improved device efficiency. The V_{oc} in these devices changes just a little, which indicates that the $V_{\rm oc}$ obtained has almost achieved its limit. The FF value reflects the fraction of photogenerated charge carriers, however, the FFs in this work are not very high. Further optimisation of the electrodes and device performance are underway to gain more information.

Conclusion

A new type of 2,1,3-benzothiadiazole (BT) acceptor with a conjugated aryl-vinylene side chain has been designed and used to build efficient low bandgap (LBG) photovoltaic copolymers. Three 2D-like donor (D)-acceptor (A) conjugated copolymers based on benzo[1,2-b:3,4-b']dithiophene and the resulting new BT derivatives, PBDBT1, PBDBT2 and PBDBT3, were synthesised by Stille coupling polymerisation. Their optical and electrochemical properties can be facilely affected by adjusting the structures of the conjugated aryl-vinylene side chains attached to the BT units. UV/ Vis absorption and cyclic voltammetry measurements show that PBDBT3 has the best light harvesting and smallest bandgap of the three copolymers. The basic electronic structures of the D-A model compounds of these copolymers were also studied by DFT calculations at the B3LYP/6-31G* level of theory. PSCs based on these copolymers were fabricated with a typical structure of ITO/PEDOT:PSS/copolymer:PCBM/Ca/Al and illuminated with AM1.5G at 100 mW cm⁻². The results showed that **PBDBT3** devices have higher efficiencies of 1.92 and 2.17% compared with the **PBDBT1** and **PBDBT2** devices using PC₆₁BM and $PC_{71}BM$ as acceptors, respectively. The results presented herein indicate that these copolymers are promising candidates for roll-to-roll manufacturing of PSCs. Suitable electronic, optical and photovoltaic properties of BT-based copolymers can be achieved by fine-tuning the structures of the aryl-vinylene side chains for application in PSCs.

Experimental Section

Materials and instruments: NMR spectra were recorded on a Bruker Avance-400 spectrometer with [D]chloroform as the solvent and tetramethylsilane as the internal standard. Cyclic voltammetry was performed on a CHI660 potentiostat/galvanostat electrochemical workstation at a scan rate of 50 $mV\,s^{-1}$ with a platinum wire counter electrode and a Ag/AgCl reference electrode in an anhydrous nitrogen-saturated 0.1 м acetonitrile solution of tetrabutylammonium perchlorate (nBu₄NClO₄). The copolymers were coated on platinum plate working electrodes from dilute chloroform solutions. UV/Vis spectra were obtained on a Carry 300 spectrophotometer. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a TA Instrument Model SDT Q600 simultaneous TGA/DSC analyser at a heating rate of 10°Cmin⁻¹ and under a N2 flow rate of 90 mL min-1.

Copolymer and [6,6]phenyl-C₆₁-butyric acid methyl ester or [6,6]phenyl- $C_{71}\mbox{-butyric}$ acid methyl ester (PC_{61}BM or PC_{71}BM) were dissolved in anhydrous 1,2-dichlorobenzene (DCB) in the desired blend ratio. The blend solution was heated on a magnetic hotplate stirrer at 70 °C for 2 h. followed by stirring at 40 °C overnight. The final concentration of the polymer in the blend ranged from 8–10 mg mL⁻¹. Devices were prepared on indium tin oxide (ITO) patterned glass substrates.

All reagents were purchased from Aladdin Reagent Co., Alfa Aesar Co. and Aldrich Chemical Co. unless stated otherwise. Commercial chemicals were used without further purification. PC61BM and PC71BM were purchased from Nano-C, Inc. 4-Dodecyloxybenzaldehyde, 2-dodecyl-5-thiophenecarbaldehyde and 2,6-bis(trimethyltin)-4,8-bis(dodecyloxy)benzo[1,2-b:3,4-b]dithiophene were synthesised according to the literature.^{[8a,}

The ITO patterned glass substrates were first sonicated in a detergent (Hellmanex) bath for 30 min, followed by two rounds of sonication in deionised water for 10 min. This was followed by successive sonication in acetone and isopropanol for 15 and 20 min, respectively. The substrates were dried under flowing nitrogen and then placed in an oven at 80°C for 1 h. The substrates were subjected to UV ozone treatment for 10 min before a PEDOT:PSS (CLEVIOS P VP Al 4083) layer of 40-45 nm thickness was spin-coated onto the ITO surface. The PEDOT:PSS-coated substrates were then annealed at 120 °C for 10 min. Next, the active layer was spin-coated in an inert glovebox (N2 atmosphere). Lastly, 25 nm of calcium and 80 nm of aluminium were deposited on the active layer by

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thermal evaporation under vacuum at 10⁻⁶ Torr. The active area of the device was 0.09 cm². The thickness of the film was measured by using a surface profiler (KLA-Tencor P10 surface profiler). Current density-voltage (J-V) measurements were carried out in an inert environment (MBraun glovebox, N₂ atmosphere) under 1 Sun (AM1.5G) conditions by using a solar simulator (SAN-EI Electric XES-301S 300W Xe Lamp JIS Class AAA) at an intensity of 100 mW cm⁻². The external quantum efficiency (EQE) as a function of wavelength was measured with a home-built setup consisting of an Oriel 300-W Xe lamp in combination with an Oriel Cornerstone 130 monochromator and a SRS 810 lock-in amplifier (Stanford Research Systems). The number of photons incident on the device was calculated for each wavelength by using a calibrated silicon diode as reference.

2-Dodecanoylthiophene (1): A solution of thiophene (2 g, 0.023 mol) in freshly distilled methylene dichloride (70 mL) was added to a 250 mL flask under an argon atmosphere. Dodecanoyl chloride (5.46 g, 0.026 mol) was then slowly added dropwise to the solution. The mixture was stirred at room temperature for 30 min and then cooled to 0°C. Subsequently, anhydrous AlCl₃ (5.46 g, 0.026 mol) was added in batches. The mixture was warmed to room temperature and stirred overnight. Then 2M hydrochloric acid (100 mL) was added to end the reaction and the mixture was extracted with CHCl₂ (3×100 mL). The combined organic layers were dried over MgSO4 and the solvents were removed by rotary evaporation. Lastly, the crude compound was purified by column chromatography (silica gel; eluent: CH2Cl2/hexane, 1:1, v/v) and isolated as a pale-yellow oil. Yield: 5.32 g (86%); ¹H NMR (400 MHz, CDCl₃): $\delta =$ 7.70 (d, 1H), 7.61 (d, 1H), 7.12 (t, 1H), 2.88 (t, 2H), 1.78-1.72 (m, 2H), 1.35–1.26 (m, 16H), 0.89–0.86 ppm (t, 3H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 193.46, 144.56, 133.25, 131.62, 128.02, 39.45, 31.92, 29.63, 29.50, 29.45,$ 29.36, 24.81, 22.70, 14.12 ppm; HRMS (EI⁺): m/z calcd for C₁₆H₂₆OS: 266.1704 $[M^+]$; found: 266.1702; elemental analysis calcd (%) for C₁₆H₂₆OS: C 72.12, H 9.84, S 12.03; found: C 72.08, H 9.86, S 12.08.

2-Dodecanoyl-5-thiophenecarbaldehyde (2): A mixture of 2-dodecanoylthiophene (1; 1.33 g, 5 mmol), N,N-dimethylformamide (1 mL) and 1,2-dichloroethane (8.4 mL) was cooled to 0°C in an ice bath. Phosphorus oxychloride (1.2 mL) was slowly added dropwise. The reactant solution was then heated at reflux overnight. After cooling the mixture to room temperature, a saturated aqueous solution of acetic acid (20 mL) was added. The mixture was stirred for a further few hours and extracted with CH₂Cl₂ (3×100 mL). The combined organic layers were dried over MgSO4 and the solvents removed by rotary evaporation. The residue was purified by column chromatography (silica gel; eluent: CH2Cl2/hexane, 1:1.5, v/v) to give pure compound 2 as a pale-yellow oil. Yield: 1.23 g (83.4%); ¹H NMR (400 MHz, CDCl₃): $\delta = 9.67$ (s, 1 H), 7.56 (d, 1 H), 7.19 (d, 1H), 2.56 (t, 2H), 1.78-1.72 (m, 2H), 1.48-1.27 (m, 18H), 0.88 ppm (t, 3H); 13 C NMR (100 MHz, CDCl₃): $\delta = 189.9$, 141.64, 138.2, 132.4, 130.6, 127.1, 31.9, 29.7, 29.6, 29.4, 29.3, 28.6, 27.8, 22.7, 14.1 ppm; HRMS (EI⁺): m/z calcd for C₁₇H₂₆O₂S: 294.1654 [M⁺]; found: 294.1658; elemental analysis calcd (%) for $C_{17}H_{26}O_2S$: C 69.34, H 8.90, S 10.89; found: C 69.37, H 8.94, S 10.96.

4,7-Dibromo-5-methyl-2,1,3-benzothiadiazole (3): A solution of 5-methyl-2,1,3-benzothiadiazole (3 g, 19.97 mmol) in 47 $\%~HBr~(37.5\,mL)$ was heated to 125°C, and then bromine (3.06 mL, 59.91 mmol) in HBr (3 mL) was slowly added dropwise. The mixture was stirred for 6 h and then cooled to room temperature. A saturated sodium bisulfite aqueous solution was then added to remove the excess bromine. The precipitate was filtered and recrystallised in ethanol to afford pure compound 3 as a pale-yellow solid. Yield: 5.08 g (82.6 %); m.p. $150-151 \degree$ C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.76$ (s, 1 H), 2.61 ppm (s, 3 H); ¹³C NMR (100 MHz, CDCl₃): $\delta = 153.42$, 151.53, 140.42, 135.14, 114.21, 112.60, 22.64 ppm; HRMS (EI⁺): m/z calcd for C₇H₄N₂SBr₂: 305.8462 [M⁺]; found: 305.8467; elemental analysis calcd (%) for C₇H₄N₂SBr₂: C 27.30, H 1.31, N 9.10, S 10.41; found: C 27.35, H 1.38, N 9.16, S 10.46.

4,7-Dibromo-5-bromomethyl-2,1,3-benzothiadiazole (4): A mixture of compound 3 (4.49 g, 14.6 mmol), benzoyl peroxide (BPO; 90 mg, 0.39 mmol) and N-bromosuccinimide (NBS; 2.6 g, 14.6 mmol) in tetrachloromethane (86 mL) was heated at reflux for 17 h under an argon atmosphere. The solution was filtered and the filtrate concentrated by

rotary evaporation. The residues were purified by recrystallisation in tetrachloromethane to give pure compound 4 as a pale-yellow solid. Yield: 3.78 g (67%); m.p. 159–160°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.96$ (s, 1 H), 4.74 ppm (s, 2 H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.36, 152.52, 141.21, 135.55, 115.10, 113.23, 24.58 ppm; HRMS (EI+): m/z calcd for C₇H₃N₂SBr₃: 383.7567 [*M*⁺]; found: 383.7562; elemental analysis calcd (%) for C₇H₃N₂SBr₃: C 21.73, H 0.78, N 7.24, S 8.29; found: C 21.66, H 0.83, N 7.27, S 8.34.

(4,7-Dibromo-2,1,3-benzothiadiazol-5-ylmethyl)phosphonic acid diethyl ester (5): A solution of compound 4 (4.06 g, 10.49 mmol) in triethyl phosphite (20 mL) was heated at reflux for 12 h. Excess triethyl phosphite was removed by vacuum distillation. The residue was purified by column chromatography (silica gel; eluent: ethyl acetate) to afford pure compound 5 as a white solid. Yield: 1.95 g (41.1%); m.p. 112-114°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.95$ (d, 1H), 4.15–4.11 (d, 4H), 3.59– 3.54 (d, 2H), 1.32–1.29 ppm (t, 6H); $^{13}{\rm C}\,{\rm NMR}$ (100 MHz, CDCl₃): $\delta =$ 153.4, 151.9, 135.9, 134.8, 115.3, 136.1, 62.6, 34.6, 33.2 ppm; HRMS (EI+): m/z calcd for C₁₁H₁₃N₂O₃SPBr₂: 441.8751 [*M*⁺]; found: 441.8755; elemental analysis calcd (%) for C11H13N2O3SPBr2: C 29.75, H 2.95, N 6.31, S 7.22; found: C 29.79, H 2.99, N 6.36, S 7.28.

4,7-Dibromo-5-(5-dodecyl-2-thienylvinyl)-2,1,3-benzothiadiazole (6a): Sodium methoxide (0.12 g, 2.1 mmol) was added slowly to a mixture of compound 5 (0.85 g, 1.9 mmol) in N,N-dimethylformamide (7 mL) at 0°C. After stirring for 5 min, 2-dodecyl-5-thiophenecarbaldehyde (0.54 g, 1.9 mmol) was added dropwise. The mixture was stirred for another 4 h and then poured into saturated brine (100 mL). The solution was extracted with CHCl₂ (3×100 mL) and the combined organic layers were dried over MgSO₄. The solvents were evaporated to give the crude compound. After purification by column chromatography (silica gel; eluent: CH₂Cl₂/ hexane, 1:1.5, v/v), compound **6a** was obtained as a greenish vellow solid. Yield: 0.69 g (63.5%); m.p. 111–112°C; ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.14 (s, 1H), 7.35-7.28 (t, 2H), 7.06 (d, 1H), 6.74 (d, 1H), 2.83 (t, 2H), 1.71 (t, 2 H), 1.36–1.23 (m, 18 H), 0.88 ppm (t, 3 H); ¹³C NMR (100 MHz, $CDCl_3$): $\delta = 154.0, 151.9, 148.6, 139.3, 138.3, 130.2, 129.1, 128.3, 125.2,$ 122.8, 113.4, 112.7, 31.9, 31.4, 30.6, 29.6, 29.5, 29.1, 22.7, 14.1 ppm; HRMS (EI⁺): m/z calcd for C₂₄H₃₀N₂S₂Br₂: 568.0217 [M⁺]; found: 568.0213; elemental analysis calcd (%) for C24H30N2S2Br2: C 50.53, H 5.30, N 4.91, S 11.24; found: C 50.48, H 5.24, N 4.94, S 11.26.

4,7-Dibromo-5-(5-dodecanoyl-2-thienylvinyl)-2,1,3-benzothiadiazole (6b): Compound 6b was obtained as a yellow solid in a yield of 77% from the reaction of 5 with 2-dodecanoyl-5-thiophenecarbaldehyde (2) similar to the procedure described for 6a. M.p. 88-89°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.90$ (s, 1 H, Ph-H), 7.50 (d, 1 H), 7.29 (d, 1 H), 7.22 (d, 1 H), 7.10 (d, 1H), 2.79 (m, 2H), 1.66 (m, 2H), 1.49-1.27 (m, 16H), 0.86 ppm (d, 3H); 13 C NMR (100 MHz, CDCl₃): $\delta = 152.9$, 151.0, 139.5, 137.5, 137.0, 135.2, 131.6, 129.4, 127.9, 127.3, 126.0, 125.9, 112.7, 30.9, 30.4, 28.8, 28.7, 28.6, 28.4, 28.3, 28.2, 24.6, 21.7, 13.1 ppm; HRMS (EI+): m/z calcd for $C_{24}H_{28}N_2OS_2Br_2$: 582.0010 [*M*⁺]; found: 582.0013; elemental analysis calcd (%) for C24H28N2OS2Br2: C 49.32, H 4.83, N 4.79, S 10.97; found: C 49.35, H 4.86, N 4.82, S 11.05.

4,7-Dibromo-5-(4-dodecyloxyphenylvinyl)-2,1,3-benzothiadiazole (6c): Compound 6c was obtained as a yellow solid in a yield of 54% from the reaction of 5 with 4-dodecyloxybenzaldehyde similar to the procedure described for **6a**. M.p. 124–125 °C; ¹H NMR (400 MHz, CDCl₃): $\delta = 7.67$ (s, 1H), 7.11 (d, 2H), 6.94 (d, 1H), 6.85 (d, 1H), 6.76 (d, 2H), 3.93 (t, 2H), 1.76 (t, 2 H), 1.45–1.25 (m, 18 H), 0.87 ppm (t, 3 H); $^{13}\mathrm{C}\,\mathrm{NMR}$ (100 MHz, $CDCl_3$): $\delta = 160.2$, 138.8, 134.9, 134.6, 134.1, 130.6, 130.5, 128.8, 128.2, 125.0, 122.7, 115.0, 114.6, 113.4, 68.2, 31.9, 29.7, 29.6, 29.4, 29.2, 26.1, 22.7, 14.1 ppm; HRMS (EI⁺): *m/z* calcd for C₂₆H₃₂N₂OSBr₂: 578.0602 [*M*⁺]; found: 578.0605; elemental analysis calcd (%) for $C_{26}H_{32}N_2OSBr_2$: C 53.80, H 5.56, N 4.83, S 5.52; found: C 53.85, H 5.62, N 4.88, S 5.59.

4,7-Bis(4-dodecyl-2-thienyl)-5-(5-dodecyl-2-thienylvinyl)-2,1,3-benzothiadiazole (7a): A solution of compound 6a (1.83 g, 3.2 mmol) and 3-dodecyl-5-(tributylstannyl)thiophene (4.72 g, 8.7 mmol) in freshly distilled THF (32 mL) was degassed. The mixture was heated at reflux under an argon atmosphere and then [PdCl₂(PPh₃)₂] (45 mg, 0.06 mmol) was added. After 12 h, the THF was removed by vacuum distillation. The residue was purified by column chromatography (silica gel; eluent: CH2Cl2/



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hexane, 1:3, v/v) to give pure compound **7a** as a brick-red solid. Yield: 2.27 g (78%); m.p. 87–88°C; ¹H NMR (400 MHz, CDCl₃): δ =8.13 (s, 1H), 8.00 (s, 1H), 7.37–7.33 (d, 1H), 7.28 (s, 1H), 7.22 (s, 1H), 7.19 (s, 1H), 7.07 (s, 1H), 6.98 (d, 1H), 6.71 (d, 1H), 2.79 (t, 2H), 2.71 (t, 4H), 1.73–1.66 (m, 6H), 1.37–1.26 (m, 54H), 0.88 ppm (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ =155.7, 151.7, 147.1, 144.4, 143.1, 140.4, 138.7, 136.1, 135.9, 132.1, 129.4, 127.3, 126.3, 125.7, 125.1, 124.9, 124.4, 123.3, 122.7, 121.6, 31.9, 31.6, 30.7, 30.6, 30.5, 29.8, 29.7, 29.6, 29.5, 29.4, 29.2, 22.7, 14 ppm; HRMS (MALDI): *m*/*z* calcd for C₅₆H₈₄N₂S₄: 913.5595 [*M*+H]⁺; found: 913.5588; elemental analysis calcd (%) for C₅₆H₈₄N₂S₄: C 73.63, H 9.27, N 3.07, S 14.04; found: C 73.66, H 9.33, N 3.14, S 14.10.

4,7-Bis(4-dodecyl-2-thienyl)-5-(5-dodecanoyl-2-thienylvinyl)-2,1,3-benzo-thiadiazole (7b): Compound **7b** was obtained as a red oil in a yield of 74% from the reaction of **6b** with 3-dodecyl-5-(tributylstannyl)thiophene similar to the procedure described for **7a**. ¹H NMR (400 MHz, CDCl₃): δ =7.99 (d, 1 H), 7.95 (s, 1 H), 7.38 (d, 1 H), 7.23 (t, 1 H), 7.17 (m, 2 H), 7.10 (m, 1 H), 7.06–7.02 (m, 2 H), 2.72–2.61 (m, 6 H), 1.70 (m, 6 H), 1.36–1.26 (m, 52 H), 0.92 ppm (t, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ =155.8, 151.8, 151.7, 144.4, 143.2, 141.0, 138.8, 138.5, 136.6, 135.7, 131.8, 130.4, 129.9, 129.5, 128.5, 128.0, 127.7, 126.8, 124.4, 122.6, 121.6, 32.0, 31.2, 30.7, 30.6, 30.4, 29.9, 29.7, 29.6, 29.5, 29.4, 29.3, 28.3, 28.2, 26.8, 22.7, 14.2 ppm; HRMS (MALDI): *m*/*z* calcd for C₅₆H₈₂N₂OS₄: 927.5388 [*M*+H]⁺; found: 927.5392; elemental analysis calcd (%) for C₅₆H₈₂N₂OS₄: C 72.52, H 8.91, N 3.02, S 13.83; found: C 72.49, H 8.93, N 3.06, S 13.86.

4,7-Bis(4-dodecyl-2-thienyl)-5-(4-dodecyloxyphenylvinyl)-2,1,3-benzothiadiazole (7 c): Compound **7c** was obtained as a brick-red solid in a yield of 76% from the reaction of **6c** with 3-dodecyl-5-(tributylstannyl)thiophene similar to the procedure described for **7a**. M.p. 91–93°C; ¹H NMR (400 MHz, CDCl₃): δ =8.20 (s, 1H), 8.01 (s, 1H), 7.45 (t, 2H), 7.41 (s, 1H), 7.24 (d, 2H), 7.18 (s, 1H), 7.07 (s, 1H), 6.90 (d, 2H), 3.98 (t, 2H), 2.74–2.68 (m, 4H), 1.80–1.69 (m, 6H), 1.46–1.26 (m, 54H), 0.89–0.86 ppm (m, 9H); ¹³C NMR (100 MHz, CDCl₃): δ =159.4, 155.8, 151.7, 144.4, 143.1, 138.8, 136.7, 136.0, 131.9, 131.8, 129.6, 129.4, 128.2, 126.3, 124.7, 124.5, 123.2, 122.5, 121.6, 31.9, 30.7, 30.6, 30.5, 29.7, 29.6, 29.5, 29.4, 29.3, 26.1, 22.7, 14.1 ppm; HRMS (MALDI): *m*/*z* calcd for C₅₈H₈₆N₂OS₃: 923.5980 [*M*+H]⁺; found: 923.5975; elemental analysis calcd (%) for C₅₈H₈₆N₂OS₃: C 75.43, H 9.39, N 3.03, S 10.42; found: C 75.47, H 9.44, N 3.08, S 10.49.

4,7-Bis(5-bromo-4-dodecyl-2-thienyl)-5-(5-dodecyl-2-thienylvinyl)-2,1,3-

benzothiadiazole (8a): NBS (0.56 g, 3.12 mmol) was added to a solution of compound 7a (1.43 g, 1.56 mmol) in chloroform (25 mL). The mixture was then stirred in the dark for 4 h at room temperature. The solvent was removed by vacuum distillation. The residue was purified by column chromatography (silica gel; eluent: CH2Cl2/hexane, 1:8, v/v) to give pure compound 8a as a red solid. Yield: 1.15 g (69%); m.p. 60-61°C; ¹H NMR (400 MHz, CDCl₃): $\delta = 8.02$ (s, 1 H), 7.81 (s, 1 H), 7.33 (d, 1 H), 7.18 (d, 1H), 7.07 (s, 1H), 6.99 (d, 1H), 6.73 (d, 1H), 2.80 (t, 2H), 2.65 (t, 4H), 1.70–1.65 (m, 6H), 1.37–1.26 (m, 54H), 0.87 ppm (t, 9H); ¹³C NMR(100 MHz, CDCl₃): $\delta = 152.7$, 150.9, 144.7, 142.4, 141.6, 140.2, 138.8, 133.3, 132.5, 131.9, 131.4, 124.0, 123.2, 122.9, 122.8, 114.5, 111.7, 110.8, 38.0, 24.8, 32.0, 31.5, 30.4, 30.1, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.7, 27.9, 22.7, 14.1 ppm; HRMS (MALDI-TOF): m/z calcd for $C_{56}H_{82}N_2S_4Br_2$: 1069.3806 [*M*+H]⁺; found: 1069.3811; elemental analysis calcd (%) for $C_{56}H_{82}N_2S_4Br_2$: C 62.78, H 7.71, N 2.61, S 11.97; found: C 62.83, H 7.75, N 2.66, S 12.05.

$\label{eq:2-thienyl} \textbf{4,7-Bis} (5-bromo-4-dodecyl-2-thienyl)-5-(5-dodecanoyl-2-thienylvinyl)-}$

2,1,3-benzothiadiazole (8b): Compound **8b** was obtained as a red solid in a yield of 73% from the reaction of **7b** with NBS similar to the procedure described for **8a**. M.p. 39–40 °C; ¹H NMR (400 MHz, CDCl₃): δ = 7.84 (d, 1 H), 7.71 (d, 1 H), 7.49–7.41 (dd, 1 H), 7.37–7.34 (d, 1 H), 7.13 (m, 1 H), 7.10–7.05 (m, 2 H), 2.67–2.61 (m, 6 H), 1.65–1.61 (m, 6 H), 1.37–1.25 (m, 52 H), 0.87 ppm (t, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 155.3, 151.5, 151.3, 143.1, 142.1, 140.9, 138.4, 138.1, 136.7, 135.6, 131.5, 131.2, 129.9, 128.6, 127.8, 127.3, 126.9, 125.6, 124.2, 123.0, 112.0, 31.9, 31.2, 30.3, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.3, 22.7, 14.1 ppm; HRMS (MALDI-TOF): *m*/*z* calcd for C₅₆H₈₀N₂OS₄Br₂: 1083.3598 [*M*+H]⁺; found: 1083.3592; elemental analysis calcd (%) for

 $C_{56}H_{80}N_2OS_4Br_2\colon$ C 61.97, H 7.43, N 2.58, S 11.82; found: C 61.93, H 7.41, N 2.63, S 11.88.

4,7-Bis(5-bromo-4-dodecyl-2-thienyl)-5-(4-dodecyloxyphenylvinyl)-2,1,3-benzothiadiazole (8 c): Compound **8c** was obtained as a red solid in a yield of 73% from the reaction of **7c** with NBS similar to the procedure described for **8a**. M.p. 52–54 °C; ¹H NMR (400 MHz, CDCl₃): δ = 8.10 (s, 1 H), 7.82 (s, 1 H), 7.46 (d, 2 H), 7.36 (d, 1 H), 7.23 (d, 1 H), 7.09 (s, 1 H), 6.91 (d, 2 H), 3.98 (t, 2 H), 2.64 (t, 4 H), 1.80 (t, 2 H), 1.69–1.63 (m, 4 H), 1.47–1.25 (m, 54 H), 0.87 ppm (t, 9 H); ¹³C NMR (100 MHz, CDCl₃): δ = 159.0, 152.1, 151.4, 142.9, 139.3, 138.3, 137.9, 137.2, 135.5, 132.5, 130.5, 129.2, 128.1, 127.7, 126.8, 124.2, 118.3, 118.2, 113.8, 110.8, 68.3, 35.5, 32.0, 31.9, 29.8, 29.7, 29.5, 29.4, 29.3, 29.1, 26.5, 26.2, 22.9, 22.7, 14.1 ppm; HRMS (MALDI-TOF): *m*/*z* calcd for C₅₈H₈₄N₂OS₃Br₂: 1079.4191 [*M*+H]⁺; found: 1079.4183; elemental analysis calcd (%) for C₅₈H₈₄N₂OS₃Br₂: C 64.42, H 7.83, N 2.59, S 8.90; found: C 64.46, H 7.85, N 2.67, S 8.99.

PBDBT1: 2,6-Bis(trimethyltin)-4,8-bis(dodecyloxy)benzo[1,2-b:3,4-b]dithiophene (0.265 mg, 0.3 mmol) and compound 8a (0.321 g, 0.3 mmol) were dissolved in toluene (15 mL). The solution was flushed with argon for 10 min and then [Pd₂dba₃] (5.5 mg, 2 mol%) and P(o-tolyl)₃ (7.3 mg, 8%) were added to the flask. The flask was purged three times by successive vacuum and argon filling cycles. The polymerisation reaction mixture was heated at 110 °C with stirring for 72 h under an argon atmosphere. 2-Tributylstannylthiophene (23.7 µL) was added to the reaction and then after 2 h, 2-bromothiophene (7.5 µL) was added. The mixture was stirred overnight to complete the end-capping reaction. It was then cooled to room temperature and then slowly poured into methanol (350 mL). The precipitate was filtered and washed with methanol and hexane in a Soxhlet apparatus to remove oligomers and catalyst residue. Finally, the polymer was extracted with chloroform. The solution was condensed by evaporation and precipitated into methanol. The polymer was collected as a dark-purple solid. Yield: 0.27 g (73 %); ¹H NMR (400 MHz, CDCl₃): $\delta =$ 8.11-8.05 (br, 2H), 7.52 (br, 2H), 7.33 (br, 3H), 6.98 (br, 1H), 6.70 (br, 1H), 4.28 (br, 4H), 2.93-2.65 (br, 6H), 1.86-1.64 (br, 10H), 1.19 (br, 90 H), 0.78 ppm (br, 15 H); 13 C NMR (100 MHz, CDCl₃): $\delta = 152.8$, 150.8, 148.8, 148.0, 147.1, 145.4, 143.3, 143.1, 140.8, 139.6, 137.2, 135.6, 134.7, 133.2, 132.7, 131.5, 131.3, 130.8, 129.2, 126.3, 125.7, 124.4, 123.0, 122.0, 117.6, 114.0, 110.8, 73.0, 30.9, 30.6, 30.0, 29.7, 28.7, 28.4, 28.2, 25.2, 21.7, 13.0 ppm; IR (KBr): v=2923, 2851, 2340, 1638, 1458, 1384, 1261, 1116, 800, 621 cm⁻¹; elemental analysis calcd (%) for $(C_{90}H_{134}N_2O_2S_6)_n$: C 73.61, H 9.20, N 1.91, S 13.10; found: C 73.18, H 9.33, N 2.12, S 13.32.

PBDBT2: Copolymer **PBDBT2** was obtained as a dark-purple solid in a yield of 80% from the reaction of **8b** with 2,6-bis(trimethyltin)-4,8-bis(-dodecyloxy)benzo[1,2-*b*:3,4-*b*]dithiophene similar to the procedure described for copolymer **PBDBT1.** ¹H NMR (400 MHz, CDCl₃): δ =8.01 (br, 2H), 7.50 (br, 2H), 7.41 (br, 3H), 7.07–7.00 (br, 2H), 4.28 (br, 4H), 2.94–2.65 (br, 6H), 1.87–1.76 (br, 10H), 1.18 (br, 90H), 0.80 ppm (br, 15H); ¹³C NMR (100 MHz, CDCl₃): δ =154.4, 152.8, 152.0, 148.8, 145.6, 145.2, 144.8, 144.0, 142.9, 139.7, 138.6, 137.3, 136.9, 134.9, 134.0, 133.3, 132.8, 131.1, 130.8, 130.0, 129.0, 128.4, 127.6, 127.4, 126.8, 124.1, 123.3, 122.0, 121.2, 117.8, 112.4, 73.0, 30.9, 30.0, 29.7, 28.7, 28.4, 25.2, 21.7, 13.1 ppm; IR (KBr): $\tilde{\nu}$ =2922, 2850, 2340, 1742, 1637, 1569, 1459, 1363, 1261, 1101, 1049, 798, 619 cm⁻¹; elemental analysis calcd (%) for (C₀₀H₁₃₂N₂O₃S₆)_n: C 72.92, H 8.98, N 1.89, S 12.98; found: C 72.49, H 9.16, N 2.02, S 13.14.

PBDBT3: Copolymer **PBDBT3** was obtained as a dark-purple solid in a yield of 91% from the reaction of **8**c with 2,6-bis(trimethyltin)-4,8-bis(-dodecyloxy)benzo[1,2-*b*:3,4-*b*]dithiophene similar to the procedure described for copolymer **PBDBT1**. ¹H NMR (CDCl₃, 400 Hz): δ = 8.19–8.05 (br, 2 H), 7.48–7.27 (br, 7 H), 6.88 (br, 2 H), 4.26–3.94 (br, 6 H), 2.94–2.84 (br, 4 H), 1.82–1.75 (br, 10 H), 1.20 (br, 90 H), 0.80 ppm (br, 15 H); ¹³C NMR (CDCl₃, 100 MHz): δ = 158.8, 152.7, 150.6, 144.4, 142.9, 142.5, 140.8, 139.8, 139.4, 137.1, 135.2, 134.8, 134.0, 133.3, 132.7, 132.1, 131.5, 131.1, 130.4, 129.4, 129.1, 127.4, 126.7, 125.4, 124.2, 121.7, 120.8, 117.5, 114.0, 111.0, 73.0, 67.2, 30.9, 30.0, 29.7, 28.7, 28.4, 21.7, 25.2, 13.1 ppm; IR (KBr): $\tilde{\nu}$ = 2923, 2852, 2340, 1637, 1458, 1382, 1262, 1168, 887, 852, 815, 622 cm⁻¹; elemental analysis calcd (%) for (C₉₂H₁₃₆N₂O₃S₅)_n: C 74.74, H 9.27, N 1.89, S 10.84; found: C 74.32, H 9.03, N 2.06, S 10.98.

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2D Photovoltaic copolymers: New benzothiadiazole acceptors with different conjugated aryl-vinylene side chains have been designed and used to build 2D-like low-bandgap copolymers (see figure). It was found that their optical and electrochemical properties can be facilely modified by changing the structures of the conjugated arylvinylene side chains. The photovoltaic properties imply that all the prepared copolymers are promising candidates for roll-to-roll manufacturing of efficient polymer solar cells.



Polymer Solar Cells -

Q. Peng,* S.-L. Lim, I. H.-K. Wong, J. Xu, Z.-K. Chen*......

Synthesis and Photovoltaic Properties of Two-Dimensional Low-Bandgap Copolymers Based on New Benzothiadiazole Derivatives with Different **Conjugated Aryl-vinylene Side Chains**

