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Synthesis and photovoltaic studies on novel fluorene based cross-conjugated donor-acceptor type polymers

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ABSTRACT

Direct arylation polymerization (DAP) is emerging as a promising green, cheap, simple, and efficient environment friendly method for synthesizing conjugated polymers without involving any organometallic reagent. We report fluorene based novel cross-conjugated alternate and random copolymers for polymer solar cells (PSCs), which were synthesized by DAP and/or Yamamoto polymerization under appropriate reaction conditions to obtain high molecular weight. These cross-conjugated polymers possess absorption maxima in the range of 490-520 nm and have narrow band gap (1.7-2.05 eV) which is suitable for bulk heterojuntion (BHJ) type organic solar cells. Among the synthesized polymers, the highest number average molecular weight (M_n) i.e. 43.1 kg mol⁻¹ was obtained for polymer P2b (poly((9H-fluoren-9-ylidene)methylene)bis((2-ethylhexyl)sulfane)-alt-4,7-di(thiophen-2-yl)benzo[c] [1,2,5]thiadiazole)), and so good polymeric films were formed for P2b. Thus, BHJ films were prepared for P2b for device performance studies and the morphology of these films was studied by atomic force microscopy (AFM). Polymer P2b was blended with the fullerene derivative [6,6]-phenyl C₇₁ butyric acid methyl ester ($PC_{71}BM$) in different ratios and under the illumination of solar simulator with Air Mass global (AM 1.5G) irradiated at 100 mW cm⁻². Power conversion efficiency (PCE) of 1.4% has been achieved for BHJs in ratio of 1:2 of P2b: PC₇₁BM in simply processed devices. This result indicates that crossconjugated polymers can be tapped as potential donors for BHJs as the PCE obtained is the highest among this type of cross-conjugated polymers.

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1. Introduction

Thin-film PSCs have various attractive features over inorganic based solar cells for the generation of renewable energy [1-3]. They have various advantages such as light weight, flexibility, good mechanical property, low cost fabrication, solution-processability and possess promising applications in large-area flexible devices [1-4]. BHJ solar cells have the active layer of conjugated organic polymers as electron donors and fullerene acceptors, which are blended together and is the most efficient cell design among all PSCs [1,3]. The development of new polymer structures and the optimization for PSCs have led to PCE as high as 10% [5]. Therefore, the design and synthesis of highly efficient low band gap novel conjugated polymers are of great importance to improve efficiency in solar cells [6]. The most efficient low band gap conjugated

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http://dx.doi.org/10.1016/j.orgel.2016.10.039 1566-1199/© 2016 Elsevier B.V. All rights reserved. polymers reported in literature are of donor-acceptor type (D-A) alternating structures [2,7,8].

Presently, such polymers are being synthesized by Kumada, Stille and Suzuki type catalytic polycondensation coupling reactions which require the preparation of organometallic monomers [9–14]. The highly toxic nature of the stannylated compounds for Stille coupling, and lesser stability of the borylated compounds for Suzuki cross-coupling strongly discourage the use of these crosscoupling methods [10,14,15]. DAP has therefore attracted a great deal of attention as an easy and non-toxic alternative to the above mentioned traditional methods [9,13,16]. It is the dehydrohalogenative coupling of aromatic compounds and aryl halides, which proceeds by C–H bond cleavage [13] of aromatic molecules with an arylpalladium carboxylate intermediate [11,17]. As the polycondensation reactions by DAP does not involve any organometallic monomer, this coupling does not produce undesirable metal-containing waste [12]. The catalyst used for DAP is phosphine free Pd-catalyst, which prevents the formation of defects in the polymers due to covalently-bonded phosphine ligands [17].

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Moreover, DAP gives higher molecular weight [16], which reduces concentration of end groups and so higher purity [12,17,18]. Also, the high molecular weight of the polymer improves the device performance [19,20].

The main chain of the low band gap polymers has electron-rich donor (D) and electron -deficient acceptor (A) moieties [21]. The band gap in the polymers is reduced by intramolecular charge transfer and their physical properties can be tuned by modifying the structures of D and A or by linking ethylene bridge [21]. The conjugated polymers possess distinct optical and electronic properties, which usually arise from a chemically tailored structure [1,8,22]. Preferably, for an ideal donor, the absorption spectra of the polymers must be broad with high intensity, so as to effectively absorb the solar radiation [3,7]. For high open-circuit voltage (V_{OC}), the donor polymer must have low HOMO level and also a good compatibility with PCBM to form a BHJ with a large interface area [4,22]. The BHJ so formed must have high hole mobility for active transportation of photo-generated charge carriers [4,21,22].

Alkylated fluorene is widely used as a donor monomer or comonomer in conjugated polymer synthesis [17]. The side alkyl chains control solubility and crystallinity of a polymer by influencing the stacking of the main chain [1,21]. In most of the reported conjugated polymers, alkyl chains are bonded to sp³ hybridized carbon atom which hinders close packing of polymer chains [21,23,24]. By inserting an ethylene bridging unit between the side chain and the main chain of D-A polymers synthesized in this study, the unwanted steric hindrance can be effectively eliminated [21]. The carbon atom in ethylene bridge has sp^2 hybridisation [23–25], due to which the side chains and main chain are coplanar and hence due to close intermolecular π - π stacking [1,24–26] main chains are closely packed which leads to smooth charge carrier hoping between the polymer chains, and high hole mobility [1,21,24]. Modified fluorene monomer (M1) is designed with thiavinylidene structure at 9-position, where sulphur atom has been introduced in the alkyl chains by ethylene bridge i.e. the alkyl group of alkylated fluorene is replaced by thioalkyl group (structure of the monomer is shown in Scheme 1). The polymers with ethylene bridge are cross-conjugated as conjugation is present in main chain as well as side chain.

This work focuses on the development of synthetic procedure of planarized cross-conjugated fluorene-type monomer and polymers [23,27]. These polymer chains are anticipated to exhibit strong solid state interaction by π -stacking due to the planar geometry of the repeat unit [23]. The effect of introduction of thioalkyl group by ethylene bridge on conjugation, solubility, band gap and device performance has been studied. Cross-conjugated D-A polymers (structure of target polymers is shown in Scheme 2 and Scheme 3), are synthesized under varied reaction conditions by polymerization of cross-conjugated fluorene derivative (M1) as donor with DTBT (M4 and M5) and alkylated DTBT (M2 and M3) as acceptor by DAP and Yamamoto polymerization [17]. We report on the optical, electrochemical and device properties of this novel class of materials.

2. Experimental section

2.1. General characterization

¹HNMR spectra were recorded on a Bruker DPX-300 spectrometer operating at 300 MHz in deuterated chloroform with tetramethylsilane (TMS) as a reference for chemical shifts. UV–vis spectra were measured on a T90 +UV/visible spectrophotometer in THF solution. Photoluminiscence (PL) spectra were measured on a SHIMADZU spectrofluorophotometer RF5301PC. Cyclic voltammograms (CV) were recorded on a Zehnar Zehnnium, potentiostat/galvanostat at a constant scan rate of 20 mV s⁻¹. For GPC measurements, THF was used as the mobile phase. GPC analysis was done on a Perkin Elmer Series 200 GPC system equipped with a refractive index detector using monodispersed polystyrene as a standard. The morphology of the active layers was investigated using Bruker AFM in tapping mode under ambient conditions.

2.2. Synthetic procedures

2.2.1. Monomer synthesis

2.2.1.1. Synthesis of ((2, 7-dibromo-9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane) (M1). 2, 7-Dibromofluorene (1 g, 3.086 mmol) was dissolved in 30 mL of dry DMSO in a dried schlenk flask under nitrogen atmosphere and the solution was cooled to



Scheme 1. Synthetic procedure for monomer M1 and structures of M2, M3, M4 and M5.

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Scheme 2. Synthetic routes for polymers P1a, P1b and P1c. The reaction conditions for the polymer synthesis are mentioned in Table 1.



Scheme 3. Synthetic routes for polymers P2a, P2b and P2c. The reaction conditions for the polymer synthesis are mentioned in Table 1.

0 °C. NaH (0.2 g, 8.33 mmol) was added very slowly to the solution as the reaction is highly exothermic followed by addition of CS_2 (0.3 mL, 3.47 mmol). As CS_2 is volatile, it was added in a little larger quantity (0.9 mL). The reaction mixture was stirred for 1 h, followed by addition of 2-ethylhexyl bromide (1.5 mL, 8.55 mmol) and stirred for further 4 h. The mixture was poured into 5% HCl solution and extracted with ethyl acetate which was dried over Na₂SO₄. The solvent was evaporated and the crude product was purified by silica gel column chromatography using hexane as eluent to obtain yellow viscous liquid as product (1.04 g, 54%). ¹HNMR (300 MHz, CDCl₃) δ : 9.09(s, 2H) 7.55(d, 2H), 7.45(d, 2H), 3.06(d, 4H), 1.64(m, 2H), 1.43–1.48(m, 16H), 0.92(t, 12H) [26].

2.2.1.2. Synthesis of 4,7-bis(4-octylthiophen-2-yl)benzo[c][1,2,5] thiadiazole(M2).

4,4,5,5-tetramethyl-2-(4-octlythiophen-2-yl)-1,3,2-dioxaborolane (0.918 g, 2.856 mmol) and 4,7-dibromo-2,1,3-benzothiadiazole (0.3 g, 1.02 mmol) were dissolved in a mixture of toluene (7.5 mL) and THF (7.5 mL) in a schlenk flask under nitrogen followed by the addition of Na₂CO₃ (0.648 g dissolved in 1 mL H₂O) and a pinch of phase transfer catalyst tetrabutylammonium bromide (TBAB). The reaction mixture was purged with nitrogen for another 10 min and then Pd(PPh₃)₄ (0.47 g, 0.04 mmol) was added. The reaction was conducted for 24 h at 110 °C. The product was extracted with chloroform and dried over Na₂SO₄. The product was purified by using silica gel column chromatography using 2% ethyl acetate/ hexane as eluent to obtain M2 (406.39 g, 76%) as bright orange solid. Melting point = 79 °C. ¹HNMR (300 MHz, CDCl₃) δ : 7.98(s, 2H), 7.83(s, 2H), 7.04(s, 2H), 2.72(t, 4H), 1.71(m, 4H), 1.35(m, 20H), 0.89(t, 6H) [28].

2.2.1.3. Synthesis of 4,7-bis(5-bromo-4-octylthiophen-2-yl)benzo[c] [1,2,5]thiadiazole(M3). M2 (0.1 g, 0.19 mmol) was dissolved in mixture of dry CHCl₃ (3 mL) and AcOH (3 mL) and the solution is

cooled to 0 °C. NBS (0.67 g, 0.38 mmol) was added and the reaction mixture was stirred overnight at room temperature in dark by covering the flask with aluminium foil. The reaction was quenched with 2 M NaOH solution and then was extracted with CHCl₃. The crude product was purified by silica gel column chromatography using 2% ethyl acetate/hexane as eluent to obtain pure product as bright orange solid (0.12 g, 96%). Melting point = 152 °C. ¹HNMR (300 MHz, CDCl₃) δ : 7.72(s, 2H), 7.70(s, 2H), 2.61(t, 4H), 1.62(m, 4H), 1.31(m, 20H), 0.83(t, 6H) [28] (see Scheme 4).

2.2.1.4. Synthesis of 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole(M4). 4,7-Dibromo-2,1,3-benzothiadiazole (0.2 g, 0.68 mmol) and thiophene (0.272 mL, 3.4 mmol) were dissolved in 40 mL dry DMF. The solution was purged with nitrogen for 10 min followed by addition of pivalic acid (0.104 g, 1.02 mmol), K₂CO₃ (0.47 g, 3.4 mmol) and catalyst Pd(OAc)₂ (0.076 g, 0.34 mmol). The reaction was conducted for 4 h at 80 °C under nitrogen atmosphere. The product was extracted with ethyl acetate and the solvent was evaporated to obtain crude product which was purified by silica gel column chromatography using 3% ethyl acetate/hexane as eluent to obtain M4, a bright orange colour solid (81.7 g, 40%). Melting point = 128 °C. ¹HNMR (300 MHz, CDCl₃) δ : 8.13(d, 2H), 7.90(s, 2H), 7.46(d, 2H), 7.23(m, 2H) [29].

2.2.1.5. Synthesis of 4,7-bis(5-bromothiophen-2-yl)benzo[c][1,2,5] thiadiazole(M5). M4 (0.07 g, 0.233 mmol) was dissolved in 3.3 mL dry CHCl₃ followed by addition of NBS (0.87 g, 0.489 mmol) at 0 °C. The reaction was conducted in dark by covering the flask with aluminium foil. The product was extracted with CHCl₃ and the solvent was evaporated to obtain crude product which was purified by silica gel column chromatography using 5% ethyl acetate/hexane as eluent to obtain M5 as bright orange solid (0.101 g, 95%). Melting point = 258 °C. ¹HNMR (300 MHz, CDCl₃) δ : 7.85(s, 2H), 7.80(d, 2H), 7.13(d, 2H) [29] (see Scheme 5).

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Scheme 5. Synthetic routes for M4 and M5.

2.2.2. Polymer synthesis

2.2.2.1. Synthesis of P1a (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-ran-4,7-bis(4-octylthiophen-2-yl)benzo[c] [1,2,5]thiadiazole). M1 (0.165 g, 0.264 mmol) and M3 (0.18 g. 0.264 mmol) were dissolved in mixture of dry DMF (1 mL) and dry toluene (1 mL) in a dried schlenk tube inside a glove box. The solution was continuously purged with nitrogen for 20 min followed by addition of 2,2'-bipyridyl (0.103 g, 0.66 mmol) and cyclooctadiene (COD) (0.8 mL, 0.66 mmol). The reaction mixture was stirred for 30 min and then Ni(COD)₂ (0.33 g, 1.2 mmol) was added. The reaction mixture was further heated with stirring at 95 °C for 48 h. Bromobenzene (0.041 g, 0.264 mmol) was added to the reaction mixture and reaction was stirred for additional 6 h at same temperature. The mixture was cooled to room temperature and poured into cold methanol (300 mL); filtered and washed with EDTA solution to remove traces of Ni metal. The polymer was then purified by soxhlet extraction and reprecipitated in cold methanol and dried after filtration to obtain purple solid. (Yield-55.5%). ¹HNMR (300 MHz, CDCl₃) δ: 9.1(s br, 2H), 8.41(d br, 2H), 8.22(d br, 2H), 7.93(s br, 2H), 7.7(s br, 2H), 3.05(d br, 2H), 2.21(d br, 2H), 1.4(s br, 20H), 0.98(m br, 30H).

2.2.2.2. Synthesis of P1b (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-alt-4,7-bis(4-octylthiophen-2-yl)benzo[c] [1,2,5]thiadiazole). A mixture of K₂CO₃ (0.11 g, 0.8 mmol), pivalic acid (0.098 g, 0.096 mmol), M1 (0.2 g, 0.32 mmol), M2 (0.168 g, 0.32 mmol) was dissolved in 3.2 mL of NMP in a dried schlenk tube in nitrogen atmosphere followed by addition of Pd(OAc)₂ (0.007 g, 0.032 mmol). The reaction mixture was stirred at 80 °C for 48 h under nitrogen atmosphere. The polymer was then precipitated in cold methanol, filtered, dried, washed with EDTA solution to remove traces of catalyst and then purified by soxhlet extraction with methanol, acetone and chloroform. The polymer soluble in chloroform was concentrated and filtered in cold methanol to obtain **P1b** as dark purple powder. (Yield-72.7%). ¹HNMR (300 MHz, CDCl₃) δ : 9.51(s br, 2H), 9.11(s br, 2H), 8.22(d br, 2H), 7.83(s br, 2H), 7.7(s br, 2H), 3.14(d br, 2H), 2.51(d br, 2H), 1.61(s br, 20H), 0.98(m br, 30H).

M5

2.2.2.3. Synthesis of P1c (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-alt-4,7-bis(4-octylthiophen-2-yl)benzo[c] [1,2,5]thiadiazole). M1 (0.120 g, 0.192 mmol) and M2 (0.1 g, 0.192 mmol) were dissolved in 1.92 mL of toluene in a dried schlenk tube under nitrogen pressure. Pivalic acid (0.0058 g, 0.0576 mmol), Cs₂CO₃ (0.25 g, 0.768 mmol), were then added to the reaction mixture while stirring followed by addition of ligand P(o-OCH₃-Ph)₃ (0.0108 g, 0.0307 mmol). The mixture was purged with nitrogen for 20 min and then Pd(OAc)₂ (0.0034 g, 0.0153 mmol) was added. The reaction was conducted at 80 °C for 48 h, which was then cooled and poured in cold methanol. The polymer was filtered, dried and washed with EDTA solution. Purification of polymer is done by soxhlet extraction with acetone and chloroform, the polymer soluble in chloroform was concentrated and reprecipitated in cold methanol to obtain a purple powder. (Yield-79.3%). %). ¹HNMR (300 MHz, CDCl₃) δ: 9.51(s br, 2H), 9.11(s br, 2H), 8.22(d br, 2H), 7.83(s br, 2H), 7.7(s br, 2H), 3.14(d br, 2H), 2.51(d br, 2H), 1.61(s br, 21H), 0.98(m br, 32H).

2.2.2.4. Synthesis of P2a (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-ran-4,7-di(thiophen-2-yl)benzo[c][1,2,5] thiadiazole). Polymer P2a was synthesized according to the procedure followed for P1a using M1 (0.2 g, 0.436 mmol), M5 (0.272 g,

0.436 mmol), 2,2'-bipyridyl (0.17 g, 1.09 mmol), COD (0.13 mL, 1.068 mmol) and Ni(COD)₂ (0.3 g, 1.09 mmol) in a mixture of dry DMF (2 mL) and dry toluene (2 mL) at 95 °C for 48 h. The product was obtained as dark purple solid. (Yield-48%). δ : 9.1(s br, 2H), 8.41(d br, 2H), 8.22(d br, 2H), 7.93(s br, 2H), 7.7(s br, 2H), 7.04(s, br, 2H), 3.05(d br, 2H), 2.21(d br, 2H), 1.4(s br, 20H), 0.98(m br, 30H).

2.2.2.5. Synthesis of P2b (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-alt-4,7-di(thiophen-2-yl)benzo[c][1,2,5] thiadiazole). Polymer P2b was synthesized according to the procedure followed for polymer P1c, using M1 (0.2 g, 0.32 mmol), M4 (0.096 g, 0.32 mmol), Pd(OAc)₂ (0.0057 g, 0.0256 mmol), P(o-OCH₃-Ph)₃(0.018 g, 0.0512 mmol), pivalic acid (0.01 g, 0.096 mmol) and Cs₂CO₃ (0.417 g, 1.28 mmol) in 3.2 mL toluene at 100 °C for 48 h. The product was obtained as purple solid. (Yield-86.1%). ¹HNMR (300 MHz, CDCl₃) δ : 9.40(s br, 2H), 9.00(s br, 2H), 8.095(d br, 2H), 7.83(s br, 2H), 7.61(s br, 2H), 7.44(s br, 2H), 3.14(d br, 2H), 1.65(s br, 10H), 0.90(m br, 20H).

2.2.2.6. Synthesis of P2c (Poly((9H-fluoren-9-ylidene)methylene) bis((2-ethylhexyl)sulfane)-alt-4,7-di(thiophen-2-yl)benzo[c][1,2,5] thiadiazole). Polymer P2c was synthesized according to the procedure followed for polymer P1c, using M1 (0.106 g, 0.17 mmol), M4 (0.051 g, 0.17 mmol), Cs₂CO₃ (0.166 g, 0.51 mmol), pivalic acid (0.017 g, 0.17 mmol), P(o-OCH₃-Ph)₃ (0.0024 g, 0.0068 mmol), Herrmann catalyst (0.003 g, 0.0034 mmol) in 0.34 mL toluene at 100 °C for 48 h. The product was obtained as purple solid. (Yield-62%). ¹HNMR (300 MHz, CDCl₃) δ : 9.49(s br, 2H), 9.10(s br, 2H), 8.19(d br, 2H), 7.93(s br, 2H), 7.71(s br, 2H), 7.54(s br, 2H), 3.20(d br, 2H), 1.65(s br, 10H), 0.91(m br, 20H).

2.3. Device fabrication and evaluation

Photovoltaic devices were fabricated according to the following procedures. The device configuration used for fabrication was glass/ indium tin oxide (ITO)/poly(3,4ethylenedioxythiphene):poly(styrenesulphonate) (PEDOT:PSS)/ active layer/Al with a pixel area of ~0.1 cm². Firstly, the patterned ITO-coated glass substrates with a conductivity of 20Ω square⁻¹, were washed with detergent solution. Then, these substrates were cleaned by sequential ultrasonic treatments with de-ionized water, acetone, and isopropyl alcohol for 20 min at every step followed by vapour treatment by isopropyl alcohol vapours. The cleaned ITOcoated glass substrates were dried in a vacuum oven at 100 °C for 30 min to remove any remaining solvents. A hole transporting layer, PEDOT:PSS (Heraeus Clevios PH-1000) was deposited on the ITO surface by spin coating at 3000 rpm for 90 s and then it was dried in a vacuum oven at 120 °C for 20 min. The thickness of PEDOT:PSS laver was ~40 nm under these conditions. The substrates were then moved to a glove box under nitrogen atmosphere. Active layer solutions were dissolved in 1,2,4-trichlorobenzene (TCB) with polymer concentration of 30 mg mL⁻¹ and then were ultra sonicated for 30 min. The solution was filtered and the active layer was spin coated on the ITO/PEDOT:PSS electrode at 1000 rpm for 90 s in the glove box with thickness of active layer of 120 nm. The active layer films were immediately annealed on the hot plate kept inside the nitrogen-filled glove box at 120 °C for 20 min. The samples were then transferred into the vacuum chamber (pressure $< 2 \times 10^{-6}$ Torr) for the deposition of the Al electrode (thickness 100 nm) on the top of the photoactive layer by thermal evaporation. The area of device was 0.1 cm² and the electrical properties of the device thus obtained were measured using the light from solar simulator equipped with a Keithley 2635A source measurement unit. The J-V characteristics of the devices were measured under Air Mass global (AM 1.5G) irradiation (intensity = 100 mW cm⁻²) from a Xenon lamp (150 W Oriel) using an aperture to define the illuminated area. The *J-V* characteristics of the solar cells were measured by testing six cells.

3. Results and discussion

3.1. Design and synthesis

The cross-conjugated monomer M1 of fluorene ((2, 7-dibromo-9H-fluoren-9-ylidene)methylene)bis((2-ethylhexyl)sulfane), was synthesized from 2,7-dibromofluorene. The fluorenyl anion was generated by using a strong base sodium hydride, which then reacted with carbon disulfide to give a ketene dithiolate, which was subjected to alkylation by ethylhexyl bromide to give monomer M1.

4,7-Bis(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT) is one of the most widely used acceptor monomer with high planarity for designing low band gap D-A polymers. DTBT is a D-A-D type with electron donating thiophene and electron withdrawing benzo[c] [1,2,5]thiadiazole group [2]. Additional alkyl chains are introduced on thiophene moiety to further improve the solubility of these polymers (alkylated DTBT) [8]. Although the alkyl chains provide solubility to the polymer, the charge transport properties are changed due to disturbance in intermolecular charge transfer between donor and acceptor units [30]. Monomer M2 (alkylated DTBT) was synthesized by Suzuki coupling of boronic ester of 3octylthiophene and 4,7-dibromo-2,1,3-benzothiadiazole using Pd(PPh₃)₄ as catalyst and Na₂CO₃ as base in THF/toluene/H₂O. M2 was then brominated to obtain monomer M3 by using *n*-bromosuccinimide in dry CHCl₃. Monomer M4 (DTBT) was synthesized by direct arylation one pot synthesis using thiophene and 4,7dibromo-2,1,3-benzothiadiazole as reactants with Pd(OAc)₂ as catalyst, K₂CO₃ as base and pivalic acid in DMF. This was brominated using n-bromosuccinimide in CHCl₃ to obtain M5. The structures of all the monomers are depicted in Scheme 1.

The target polymers are shown in Schemes 2 and 3. Random copolymers P1a and P2a were synthesized by Yamamoto polymerization in good yields. Polymers P1b, P1c, P2b and P2c were synthesized by DAP polymerization. The varied reaction conditions are mentioned in Table 1. The polymers were purified by soxhlet extraction with methanol, acetone, and CHCl₃ and then were washed with EDTA solution to remove traces of catalyst left in the product. All the polymers showed good solubility in common organic solvents such as CHCl₃, THF, toluene, and chlorobenzene. The gel permeation chromatography (GPC) measurements were done against monodisperse polystyrene standards with THF as eluent. The number average molecular weights (M_n) were found to be 10.3 kg mol⁻¹, 8.1 kg mol⁻¹, 6.0 kg mol⁻¹, 8.1 kg mol⁻¹, 43.1 kg mol⁻¹, and 8.6 kg mol⁻¹ for polymer P1a, P1b, P1c, P2a, P2b and P2c, respectively. Table 2 summarizes the molecular weight of all the polymers.

3.2. Absorption studies

UV-visible absorption spectra of the synthesized random and alternate copolymers measured in dilute THF solution and as thin films are shown in Fig. 1 and the corresponding optoelectronic properties are summarized in Table 2. The solution absorption maxima in THF ranged from 490 to 520 nm. Two distinct absorption bands were observed at around 350 nm and 500 nm, the one at 350 nm can be attributed to $\pi - \pi^*$ transitions of the conjugated backbones, whereas the one around 500 nm is due to internal charge transfer between donor and acceptor units. The solution spectra of all the polymers have almost same absorption maxima because of same chemical structure of the random copolymers and alternate copolymers. While moving from solution to film, the

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Table 1

Polymerization results of P1 (a,b and c) and P2 (a,b and c) under varied conditions.

S.No.	Polymer	Base	Catalyst	Solvent	Ligand	Temperature (°C)	Yield (%)
1	P1a	_	Ni(COD) ₂	DMF/Toluene	_	95	55.5
2	P1b	K ₂ CO ₃	Pd(OAc) ₂	NMP	-	80	72.7
3	P1c	Cs ₂ CO ₃	Pd(OAc) ₂	Toluene	P(o-OCH ₃ -Ph) ₃	80	79.3
4	P2a	_	Ni(COD) ₂	DMF/Toluene	-	95	48
5	P2b	Cs ₂ CO ₃	Pd(OAc) ₂	Toluene	P(o-OCH ₃ -Ph) ₃	100	86.1
6	P2c	Cs ₂ CO ₃	Herrmann catalyst	Toluene	P(o-OCH ₃ -Ph) ₃	100	62

Table 2

Optical and electrochemical properties a) THF solution, b) Film, c) Optical band gap, d) Electrochemical band gap, M_n is number average molecular weight and M_w is weight average molecular weight.

S.No.	Polymer	Absorption (nm)		Emission (nm)	HOMO	LUMO	E ^c _{g(opt)}	Egd	M _n	M _w	
		λ_{max}^{a}	λ_{max}^{b}	λ^{b}_{edge}	λ_{max}^{a}	(eV)		Band gap (eV)		$(kg mol^{-1})$	
1	P1a	490	522	676	645	-5.75	-3.90	1.85	1.83	10.3	15.4
2	P1b	500	534	730	659	-5.75	-4.10	1.65	1.69	8.1	10.5
3	P1c	520	534	710	634	-5.60	-3.70	1.74	1.90	6.0	6.3
4	P2a	520	506	720	648	-5.70	-3.85	1.85	1.72	8.1	10.2
5	P2b	520	546	715	638	-5.70	-3.70	1.73	2.00	43.1	67.2
6	P2c	500	514	682	625	-5.75	-3.70	1.81	2.05	8.6	10.2



Fig. 1. Absorption spectra of polymers in (A) THF solution, (B) Film on glass. (C) Emission spectra of polymers in THF solution.

absorption maxima became slightly broader and red shifted owing to the increased inter-chain interactions and π - π stacking in the solid state. The optical band gap ($E_{g(opt)}$) of these polymers was estimated from the onset absorption in the thin film and found to be in the range of 1.65–1.85 eV. The narrower $E_{g(opt)}$ can be attributed to ordered and planar structure of the conjugated structure. The emission spectra were also measured in THF solution and the maxima range from 625 to 659 nm and are summarized in Table 2.

3.3. Electrochemical properties

The electrochemical properties were studied using cyclic voltammetry. The highest occupied molecular orbital (HOMO) energies were calculated from the first oxidation onset of the cyclic voltammogram according to the equation $E_{HOMO} = -e(E_{ox} + 4.4) \text{ eV}$. The lowest unoccupied molecular orbital (LUMO) energy levels were calculated by using the equation $E_{LUMO} = -e(E_{red} - 4.4) \text{ eV}$ from the onset reduction potential. The deep lying HOMO level for

the polymers ranges from -5.60 eV to -5.75eV. This is an ideal range to ensure better air stability and greater obtainable open circuit voltage (V_{oc}) in the photovoltaic cell. The LUMO level ranges from -3.70 eV to -4.10 eV which is again fits with the required electronic levels for better device performance using PC₇₁BM as the acceptor. The band gap ranges from 1.69 eV to 2.05 eV. Table 2 summarizes the HOMO, LUMO and electrochemical band gap values of all the polymers. The cyclic voltammograms are shown in Fig. 4.

3.4. Photovoltaic properties

BHJ solar cells were fabricated for studying the photovoltaic properties of the blends. The device configuration is glass/ITO/PEDOT:PSS/P2b:PC₇₁BM/Al. PEDOT:PSS works as an electrical connector to accelerate the recombination of photogenerated charge carriers (electron and hole). The photoactive layers were composed of PC₇₁BM as acceptor and newly synthesized polymer

P2b as donor. P2b was chosen for the device fabrication because it formed good quality films due to its high molecular weight. The photovoltaic performance was optimized in different P2b:PC71BM weight ratios to achieve best PCE. Three different binary compositions of P2b and PC71BM i.e. 1:1, 1:2 and 1:3 were used. The blends were prepared by mixing a solution of P2b:PC₇₁BM in (TCB) which were then used for BHI solar cells by spin coating. After optimization studies, a weight ratio of P2b to PC₇₁BM of 1:2, a concentration of 30 mg mL⁻¹, thermal annealing at 120 °C for 20 min and with a thickness of the blend films of about 100 nm gave the best device properties. For the binary blend (1:2), a PCE of 1.4% was attained with Voc of 0.49 V, short circuit current (Jsc) of 9.6 mA cm⁻² and fill factor (FF) of 0.29. To verify the consistency of the best efficiency, six devices were fabricated on all conditions. The current densities versus voltage (I-V) characteristics of the fabricated device are displayed in Fig. 2 and their key features are summarized in Table 3. The FF values observed are quite low and the PCE can be further increased by improving the FF. The lower FFs can be attributed to



Fig. 2. Cyclic voltammograms of the polymers.

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Table 3

Summary of	of	photovoltaic	pro	perties of	of po	olymer	blend	P2b:PC7	BM.
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S.No	P2b:PC71BM	J_{sc} (mA cm ⁻²)	$V_{oc}\left(V ight)$	FF (%)	PCE (%)
1	1:1	4.3	0.48	28.9	0.6
2	1:2	9.6	0.49	29.3	1.4
3	1:3	5.4	0.53	28.9	0.8



Fig. 3. J-V characteristics of devices measured under the illumination of AM 1.5 G (100 mW cm $^{-2}$) from a solar simulator.

roughness values are 2.84 nm, 1.94 nm and 2.22 nm respectively. The film with 1:2 ratio of P2b:PC₇₁BM blend exhibited relatively smooth surface without large phase separation with lowest rms value of 1.94 nm which indicates a good miscibility between P2b and PC₇₁BM, leading to an improved device performance. The films with ratio 1:1 and 1:3 have higher rms values (2.84 and 2.22 respectively) and so they show a little larger phase separation and hence a lower device efficiency. Hence ratio of 1:2 for P2b:PC₇₁BM blend film is most desirable for better performance in PSCs.

4. Conclusions

Novel fluorene and benzothiadiazole based cross-conjugated D-A polymers with low band gap have been developed. These polymers possess ethylene bridging units between main chain and side thioalkyl chains. Ethylene bridge gives a coplanar configuration between the side chains and main chain and electron rich sulphur provides electron donating properties to the polymer. The synthesized polymers show good solubility in common organic solvents with a broad absorption band centered around 500 nm The electrochemical properties were studied and the polymers were found to have low band gap in the range of 1.7 eV–2.05 eV. Among the synthesized polymers, P2b formed a good film because of its high molecular weight and hence was used for device fabrication for solar cells. P2b:PC₇₁BM based BHJs were fabricated in different ratios by solution processing using elevated temperatures and it



Fig. 4. AFM images (10 µm × 10 µm) of P2b:PC71BM films spin coated from 1,2,4-trichlorobenzene solutions in three different ratios of (A)1:1, (B)1:2 and (C)1:3.

inappropriate morphology and improper thickness of the active layer [31,32]. The FF values may also be low because of chemical degradation of the metal-polymer interface [31,32] The FF values can be improved by smoothening the morphology of the active layer by thermal treatment or by blending with small molecules like 1,8-diiodooctane, 1,8-octanedithiol or chloronaphthalene with active layer as reported in recent literature [33]. These additives have been found to enhance the miscibility of the two components of the active layer, thereby leading to the formation of a better interpenetrating network. Variation in the thickness of the active layer can also increase FF values [32] and these will be the focus of future studies.

3.5. Morphological studies

The morphology of P2b:PC₇₁BM blend films, is closely related to the device performance of BHJ PSCs, and was investigated by AFM using tapping mode. Fig. 3 shows the AFM images of the P2b:PC₇₁BM blend films in 1,2,4-trichlorobenzene solution in three ratios i.e. 1:1, 1:2 and 1:3 with the root-mean-square (rms)

was found that the ratio of 1:2 is the most promising system and exhibited 1.4% PCE. The limited performance of the devices presented can be because of inefficient exciton dissociation or enhanced charge recombination. Further modifications in the device structure and optimization studies to smoothen the surface morphology of the photoactive layers are expected to give increased photocurrent for the devices with better efficiency.

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