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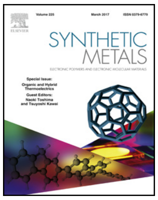

# Direct arylation polymerization approach for the synthesis of narrow band gap cyclopentadithiophene based conjugated polymer and its application in solar cell devices

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ABSTRACT

Direct arylation polymerization is a simple, cost-effective and efficient method for synthesizing conjugated polymers. The synthesis of a narrow band gap conjugated polymer, PCPDTTBT, comprising of alternating cyclopentadithiophene (CPDT) and 4,7-di(thiophen-2-yl)benzo[*c*][1,2,5] thiadiazole (TBT) units was carefully optimized by direct arylation polycondensation. The synthesized polymer has a number average molecular weight of 36.3 kg mol$^{-1}$ with a low PDI of 1.25 as measured by GPC against polystyrene standards. PCPDTTBT exhibits an absorption maximum at 617 nm in THF solution whereas in thin film, the absorption spectrum was broader and a maximum was observed at 650 nm. The HOMO, LUMO and band gap calculations were estimated using cyclic voltammetry and were found to be −5.20 eV, −3.57 and 1.63 eV, respectively. Bulk heterojunction polymer solar cells were fabricated by blending PCPDTTBT and PC$_{71}$BM in three different ratios with six cells for each ratio to optimize the efficiency. It was found that the blend ratio of 1:2 exhibited a high short-circuit current of 10.03 mA cm$^{-2}$, open-circuit voltage of 0.567 V and a power conversion efficiency of 1.86%. The morphology of the active layer was investigated by employing atomic force microscopy (AFM) in tapping mode and the film of active layer with 1:2 ratio of PCPDTTBT: PC$_{71}$BM showed most favorable morphology with less phase separation.

## 1. Introduction

Conjugated organic molecules and polymers with extended delocalized π-electrons have wide applications in optoelectronics such as solar cells, light emitting diodes, field-effect transistors etc. and are an area of intense investigation [1–14]. Polymer solar cells (PSCs) are amongst the most promising candidates for the low cost generation of renewable energy [3,5,15–18]. Conjugated polymers (CPs) have the ability to efficiently absorb the photons across the solar spectrum and possess good electrical transport properties for both holes and electrons making them suitable for use in photovoltaic cells [3–5]. Organic solar cells based on CPs and fullerene mixtures have been widely studied to attain high power conversion efficiency (PCE) in the recent past [16,19,20]. Bulk heterojunction (BHJ) cells have been found to be most efficient cell design among the different device architectures which have been developed during the last decade [4,10,15,21]. It is based on quasi-interpenetrating networks of electron donors and electron acceptors where excitons are formed, efficiently dissociated and transported to the electrodes upon irradiation in the active layer due to the formation of two percolating networks [13,17,19,22]. Extensive research has been going on aiming at increasing PCE of PSC [20]. Poly(3-hexylthiophene) (P3HT) which acts as donor is blended with [6,6]-phenyl-C$_{61}$-butyric acid methyl ester (PC$_{61}$BM) as acceptor is found to exhibit high PCE upto 4-5%, but as the absorption maxima is located at lesser values than 650 nm, it is able to harvest only a small part i.e. 22.4% of the accessible photons from the sunlight [1,16,17,21–23]. Thus, it is essential to tune the energy levels and band gap of the donor semi-conducting polymers for PSC applications [7,24]. Development of donor-acceptor type alternating copolymers is a significant approach for

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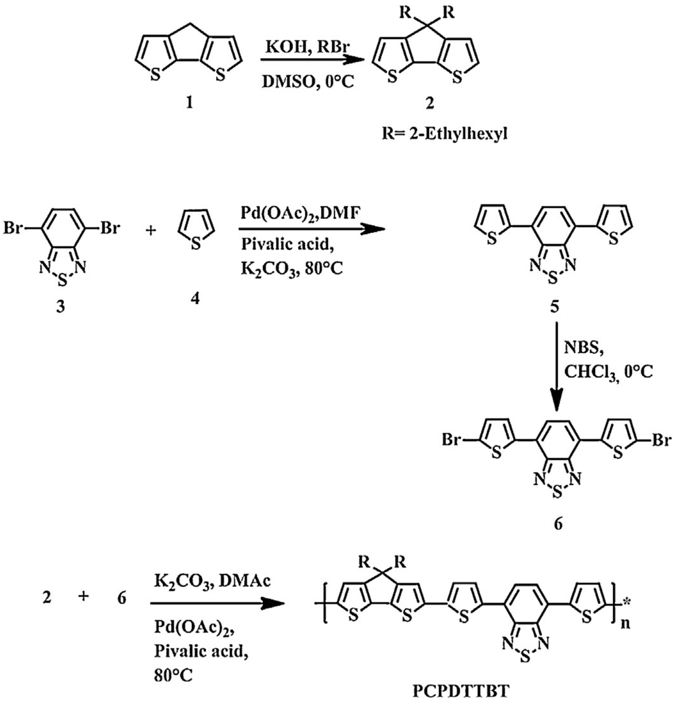
tuning the band gap [7,10,11,14,15,18,21,23]. In this approach, a low band gap is obtained due to the interactions of the (highest occupied molecular orbital) HOMO and (lowest unoccupied molecular orbital) LUMO of the electron rich and electron deficient blocks, the HOMO level of the resulting polymer is raised, whereas the LUMO level is lowered [9,16,25]. The band gap is further reduced by increasing the degree of delocalization of electrons which is achieved by increasing the coplanarity of the structure [5,24]. This can be explained by intramolecular charge transfer in excited state; here the excited electron is delocalized over electron deficient block [1,16]. The alternately arranged building blocks are in most cases synthesized by aryl–aryl cross coupling reactions using Suzuki or Stille type polycondensation which are conventional methods for polymer synthesis [2–4,6,21,26]. These polycondensation methods require organometallic reagents like organotin and organoboronates for Stille and Suzuki coupling, respectively which results in generation of highly toxic byproducts [2,6]. Also, the organometallic reagents involved often have low stability [3,6]. Moreover, synthesis of these monomers for polymerization requires tedious steps and purification of stannylated and borylated compounds is very difficult, which leads to compromise in the quality of final product [2,3,6]. Hence, it is desirable to find alternative methods to these traditional polymerization techniques [4,6,27]. One such emerging method is the direct arylation polymerization (DAP) technique which involves lesser number of synthetic steps [2,6,27]. DAP is a cross-coupling reaction involving the activation of an aromatic C—H bond. In contrast to the Suzuki and Stille type polycondensation, DAP does not involve stannyl and boron derivatized organometallic reagents [6,27]. This synthetic technique is economically sound and ecologically safe as compared to traditional cross-coupling techniques [4]. DAP takes place in presence of an inorganic base like $K_2CO_3$, $Cs_2CO_3$, KOAc and t-BuOK. Pivalic acid is also used and presence of a transition metal catalyst is required [6]. $Pd(OAc)_2$ is one of the most widely used catalyst for DAP [6,28]. A few DAP reactions require presence of a ligand particularly in the cases where C—H bond is less reactive [6]. Polar aprotic solvents such as dimethylacetamide (DMAc), DMF and NMP are widely used for DAP, but recently non-polar solvents like toluene have also been used successfully [27].

Various donor-acceptor conjugated copolymers containing fluorene, 4*H*-cyclopenta[1,2-*b*:5,4-*b*′]dithiophene (CPDT), thiophene and carbazole units as donor and benzothiadiazole, quinoxaline and thienopyrazine units as acceptor are known to show good PCE [24]. Poly[2,6-(4,4-bis[2-ethlyhexyl]-4*H*-cyclopenta[2,1-b;3,4-b]dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT) possesses a low band gap of 1.40 eV and a broad absorption ranging from 380 to 900 nm [7,29–33]. A PCE of 5.5% has been achieved using PCPDTBT in BHJ based solar cells [22,31]. One plausible approach to improve the efficiency is to incorporate planar molecular structures in the polymer backbone. CPDT based polymers show low band gap and highly planar and rigid structures which results in high carrier mobilities [5,7,24,29]. Benzothiadiazole flanked with thiophene units (TBT) is also a planar, conjugated structure with strong π–π interactions and also high electron-withdrawing effects [16]. In this contribution, the synthesis of the alternating copolymer PCPDTTBT, with electron rich alkylated CPDT monomer and electron deficient TBT monomer by direct arylation approach (Scheme 1) and its optical, electrochemical and morphological studies are presented. Although the polymer PCPDTTBT has also been synthesized earlier by Stille coupling which involves tin derivative of CPDT [21] but the DAP synthetic procedure is advantageous in terms of non-involvement of any toxic intermediates and lesser number of steps involved in the polymerization. Solar cell devices were fabricated using a blend of the PCPDTTBT as donor material and $PC_{71}BM$ as acceptor material and optimization studies with different ratios of the two as well as the effect of different additives on device efficiency are discussed.



**Scheme 1.** Synthetic pathway for the preparation of the monomers and polymer (PCPDTTBT) by direct arylation method.

## 2. Experimental

### 2.1. Materials

The precursor, 4H-cyclopenta[2,1-b:3,4-b']dithiophene, was purchased from Luminescence Technology Corporation, Taiwan. 4,7-Dibromo-2,1,3-benzothiadiazole (3) and thiophene (4) were purchased from Sigma Aldrich and Spectrochem, respectively. The monomers 4,4′-bis(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b′] dithiophene (2) and 4,7-bis(5-bromothiophen-2-yl)benzo[c] [1,2,5]thiadiazole (6) were synthesized as reported in literature [34,35]. All the synthesis was carried out under nitrogen atmosphere using dry solvents. For device fabrication, indium tin oxide (ITO) coated glass substrate (having sheet resistance 15 Ω/sq.), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS), calcium (99%) and aluminium wire (99.999% purity) were purchased from Sigma Aldrich, India. 1-chloronaphthalene were purchased from TCI Chemicals (India) Pvt. Ltd. All the chemicals purchased were used as received.

### 2.2. Measurements and characterization

$^1H$ NMR spectra were recorded on a Bruker 300 MHz spectrometer using deuterated chloroform as solvent with tetramethylsilane (TMS) as reference for chemical shifts. The number average molecular weight ($M_n$) and weight average molecular weight ($M_w$) of the polymer PCPDTTBT were measured by gel permeation chromatography (GPC) using THF as the mobile phase against polystyrene standard. GPC analysis was done on a Waters chromatography unit equipped with Waters 2414 refractive index detector. UV–vis absorption spectra were measured on T90+ UV/vis spectrophotometer. Electrochemical cyclic voltammogram (CV) was recorded on a Zehnar Zehnnium, potentiostat/