

# Random copolymers consisting of dithienylcyclopentadienone, thiophene and benzothiadiazole for bulk heterojunction solar cells

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## ABSTRACT

Novel random copolymers containing dithienylcyclopentadienone, thiophene and benzothiadiazole were synthesized and photovoltaic properties of these materials were evaluated. Thermal, structural, optical and electrochemical characterization of the synthesized copolymers was carried out. These thermally stable copolymers are solution processable unlike the homopolymer. The absorption spectra indicated that with the incorporation of alkyl chains in the thiophene moiety, the onset of absorption increases and hence band gap decreases (1.47 eV to 1.41 eV). Bulk heterojunction solar cells were fabricated with the blend of copolymer and phenyl-C61-butyric acid methyl ester (PCBM) as the active material and device parameters were extracted. The copolymer consists of alkyl thiophene exhibit higher open circuit voltage than the copolymer consisting of thiophene moiety.

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## 1. Introduction

Conducting polymers, due to their inherent semi conducting properties have been found a variety of application in the field of organic electronics [1,2]. These pi conjugated material becoming promising materials for low cost, large area flexible electronics organic photovoltaic device (OPVD) [3,4]. Bulk heterojunction solar cells are widely using configuration in of polymeric solar cells in which the active layer consists of a p type conducting polymer and an electron acceptor such as phenyl-C61-butyric acid methyl ester (PCBM) [5–7]. Thiophene, carbazole, fluorene derivatives have been used extensively as the p type conjugated material [8–11]. Selection of these conjugated polymers for organic photovoltaic application includes various factors such as light absorption, charge transportation, solubility etc [12]. The efficiency of OPVD can be enhanced by improving the above mentioned factors. Among these factors, light absorption is significant. Resolving the intrinsic absorption limit of the conjugated polymers can enhance the performance of OPVD [13]. Recently researchers have been working on the synthesis of low band gap conducting polymers consisting of donor (D) and acceptor (A) units, which can absorb light in the visible and near-infrared region of the solar spectrum [14–18].

Thiophene derivatives are extensively used as the active material component in the bulk heterojunction solar cells [19–21]. 2,5-dithienyl-3,4-(1,8-naphthylene)cyclopentadienone

(DTCPA) is a thiophene derivative where thiophene moieties acts as donor and ketone as acceptor [22]. The absorption spectrum of this conducting monomeric unit covers whole visible region and some part of near IR region of the solar spectrum [23,24]. In this donor-acceptor-donor type architecture of the molecule, fine tuning of the band gap is possible due to the intramolecular charge transfer (ICT) from the donor to the acceptor moiety. Hence, the polymers derived from DTCPA are low band gap polymers [25]. Chemical oxidative polymerization of DTCPA in presence of ferric chloride results a conducting polymer, poly-DTCPA having broad absorption and low band gap (~1.5 eV) [24]. However, like most other conducting polymers, solubility is the main issue also in the case of polyDTCPA [26].

Solubility of conducting polymers could be increased by various schemes. Copolymerization is one of the technique to improve the solubility of conducting polymers [27,28]. By combining two suitable co monomers such as one being electron donating and the other one being electron deficient moiety, low band gap solution processable copolymers are synthesized [29]. In addition to the band gap engineering, copolymerization of suitable monomeric units results conducting polymers of improved electrical, mechanical and thermal properties. Various solution processable DTCPA derivatives have been previously reported, such as a copolymer of DTCPA with benzothiadiazole (BT) which is an electron deficient moiety [25,27,30]. The other possible moiety that can be used for copolymerization is 4,7-di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (DTBT), where there are two thiophene moieties between the BT moiety. The incorporation of these two thiophene moieties with the BT units allows the synthesis of coplanar polymers [31].

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In this work, a random copolymer of DTCPA with DTBT was synthesized. In addition, to further increase the solubility, instead of DTBT, 4,7-bis(3-hexylthiophen-2-yl)benzo[c][1,2,5]thiadiazole (BHTBT) moiety was used to synthesize another copolymer DTCPA-co-BHTBT. Thermal, optical, and electrical properties of these copolymers were studied. Bulk hetero junction PV devices were fabricated with the blends of synthesized copolymers and (PCBM) as the active material.

## 2. Experimental

Monomer DTCPA was prepared by the double Knoevenagel condensation with acenaphthenequinone and di(thiophene-2-yl)propane-2-one [24]. Self condensation of thiophene acetic acid using dicyclohexylcarbodiimide (DCC) and dimethylaminopyridine (DMAP) results the intermediate compound di (thiophene-2-yl) propane-2-one (Scheme 1). 2,1,3-benzothiadiazole was synthesized from *ortho*-phenylenediamine in the presence of triethylamine and thionyl chloride. 4,7-dibromo-2,1,3-benzothiadiazole was obtained by the bromination of 2,1,3-benzothiadiazole in the presence of Br<sub>2</sub> and hydrobromic acid (HBr) (Scheme 2) [32]. Synthesis of 3-hexylthiophene (3HT) was carried out by Grignard reaction using 3-bromo thiophene [33]. Tributyl stannane derivatives of thiophene and 3HT were synthesized by the reaction of respective compounds with *n*-Butyllithium (*n*-BuLi) and tributylchlorostannane [34]. Monomers DTBT and BHTBT were synthesized by the stille coupling reaction of the tributyl stannane derivatives of the respective compound and 4,7-dibromo-2,1,3-benzothiadiazole in presence of tetrakis (triphenylphosphine) palladium catalyst (Schemes 3 and 4). Polymer and copolymers were synthesized by the chemical oxidative polymerization of the monomers in presence of anhydrous FeCl<sub>3</sub> (Scheme 5).

### 2.1. Materials

3-bromothiophene, [1,3-bis (diphenylphosphino) propane] dichloronickel(II) (Ni(dppp)Cl<sub>2</sub>), 1-bromohexane, *o*-phenylenediamine, thionyl chloride, *N*-bromosuccinimide, tetrakis (triphenylphosphine) palladium (Pd(PPh<sub>3</sub>)<sub>4</sub>), 2-thiophene-acetic acid, DCC, DMAP, tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>), and acenaphthenequinone were purchased from Sigma Aldrich and used without further purification. *n*-BuLi solution (1.6 M in hexane) was purchased from Across chemicals and used as such. Solvents DMF, dichloromethane (DCM), ethanol, chlorobenzene, and chloroform were distilled before use. Poly(3,4-ethylenedioxythiophene): polystyrene sulfonic acid (PEDOT:PSS) CLEVIOS P VP.AI 4083 was obtained from H.C. Starck Clevis GmbH, CHEMPARK

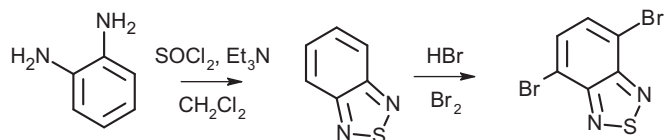
Leverkusen (Formerly Baytron). ITO coated glass plates (sheet resistance ~70–150 Ω) were purchased from Delta Technologies, Limited, USA. Phenyl-C61-butyric acid methyl ester (PCBM) was purchased from American Dye Source Inc, Canada.

### 2.2. Synthesis of di (thiophen-2-yl) propan-2-one

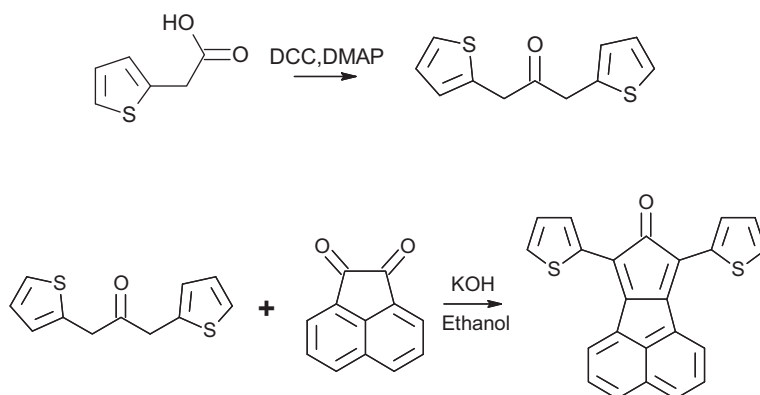
2-thiophene-acetic acid (5.0 g, 0.0352 mol) in anhydrous dichloromethane (30 mL) was added drop wise using a syringe to a stirred solution of DCC (7.6 g, 0.0368 mol) and DMAP (1.2 g, 0.0100 mol) in anhydrous dichloromethane (70 mL) at 0 °C. Reaction was continued for 12 h at room temperature in an argon atmosphere. Byproduct urea was removed by filtration. The filtrate was concentrated using rotary evaporator under reduced pressure. Di (thiophen-2-yl) propan-2-one was obtained as yellow solid by column chromatography with petroleum ether and ethyl acetate as eluting solvent. Yield=65%. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ in ppm) 7.21–7.23 (2H, d), 6.95–6.99 (2H, dd), 6.85–6.90 (2H, d), 3.99 (4H, s). HRMS (ESI, m/z): (M+Na) calculated for C<sub>11</sub>H<sub>10</sub>OS<sub>2</sub>, 245.31; found 245.00.

### 2.3. Synthesis of 2,5-dithienyl-3,4-(1,8-naphthylene)cyclopentadienone (DTCPA)

In a round bottom flask, di (thiophen-2-yl) propan-2-one (1.5 g, 6.7500 mmol) and acenaphthenequinone (1.2 g, 6.7500 mmol) in ethanol (75 mL) was refluxed. Potassium hydroxide (0.5 g) dissolved in ethanol (3 mL) was added drop wise when the reaction mixture becomes homogenous. During the addition, the solution turned to dark green color and then resulting mixture was quenched into an ice bath. Resulting dark green solid was filtered, washed with cold ethanol and hot hexane respectively and was dried under vacuum. Yield=82%. <sup>1</sup>H NMR spectrum (CDCl<sub>3</sub>, δ in ppm): 8.413–8.431 (2H, d), 7.924–7.935 (2H, dd), 7.879–7.899 (2H, d), 7.655–7.694 (2H, t), 7.494–7.509 (2H, dd), 7.216–7.259 (2H). HRMS (ESI, m/z): (M+Na) calculated for C<sub>23</sub>H<sub>12</sub>OS<sub>2</sub>, 391.46; found 391.02.



Scheme 2. Synthesis of 4,7-dibromo-2,1,3-benzothiadiazole.



Scheme 1. Synthesis of DTCPA.

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