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SYNTHESIS OF CONJUGATED COPOLYMERS FLUORENE-BASED ON THIENO-THIOPHENE FOR PHOTOVOLTAIC CELLS

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ABSTRACT

Due to the cost limitation of inorganic solar cells and the growing desire for more low-cost renewable power sources, polymer solar cells have received much interest in recent years. In this research, direct arylation polymerization was used to prepare poly(9,9-didodecylfluorene-alt-thieno[3,2-b]thiophene), **P1**, which is formed of alternating fluorene-based co-polymer units. **P1** is a donor-donor co-polymer type comprised of alternating fluorene units as a donor unit and thieno[3,2-b]thiophene as a donor unit. **P1** was identified as orange-red colour in the solid phase. TLC showed brighter under 365 nm wavelength of light for **P1**. The functional group present of **P1** was identified using FTIR, and it showed strong peaks at 2848.53 cm^{-1} and 2917.50 cm^{-1} for alkyl stretching of methylene groups. The unsymmetrical structure of **P1 with 58 hydrogens and 43 carbons** was confirmed by using ^{1}H-NMR and ^{13}C-NMR, respectively. The λ_{max} and range of adsorption of **P1** were identified, and the optical band gap value was calculated as $E_g = 2.91$ eV. The physical characteristics of **P1** were compared and discussed. Based on the chemical characteristics, **P1** has a high potential as organic photovoltaic material as UV-Vis showed a better adsorption range and lower band gap.

Keywords*: photovoltaic, fluorene based, direct arylation*

INTRODUCTION

Since the first discovery of conductive polymers in the 1970s, a large library of conjugated polymers has been synthesized and investigated. The excellent optical and electrical properties of conjugated polymers make them potential operative materials in various fields, such as photovoltaics, field-effect transistors, light-emitting diodes, and sensors [1 - 2]. Hence, it is clearly advantageous to have tailor-made conjugated polymers, which can fulfil the specific needs of such a wide range of applications. Furthermore, rational design of the conjugated backbones allows fine-tuning of physical and optoelectronic properties.

One of the most popular design strategies is incorporating electron-rich donor moiety and electron-deficient acceptor moiety alternatively in the polymer chain. This Donor-Acceptor (D-A) approach gives the possibility to adjust the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) energy levels of polymers through a proper choice of the repeating donor and acceptor units. Conjugated polymers with D-A arrangement have low bandgaps and broad absorption bands, resulting from their planar configuration that facilitates the delocalization of π-electrons along the conjugated backbone. Such low bandgap polymers are particularly attractive in Organic Photovoltaics (OPVs). D-A copolymers in Bulk-Heterojunction (BHJ) based polymer solar cells have achieved remarkable improvements in device performance. An encouraging Power Conversion Efficiency (PCE) of over 10% has been reported to develop new polymer structures and optimise device fabrication [3 - 4].

In most cases, high-performance copolymers were prepared by the Suzuki-Miyaura and Migita-Kosugi-Stille couplings. Despite being efficient and versatile, Suzuki and Stille type polycondensation suffer from several drawbacks. A tedious monomers preparation process is required. Costly organometallic reagents will be used to functionalize the monomers before couplings, and these metallated monomers can be challenging to purify. Also, the organometallic reagents used are often toxic (organotin compounds) and have low stability (organoboron compounds). The formation of highly toxic byproducts during the reaction further discourages these cross-coupling methods [5 - 6]. In this case, thiophene units were introduced as spacer moieties between the fluorene unit and the benzothiadiazole unit, as shown in **Figure 1.**

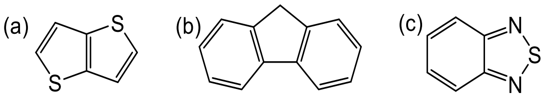


Figure 1. Chemical structure ; (a)Thieno[3,2-b]thiophene; (b) Fluorene; (c) 2,1,3-Benzothiadiazole.

Direct Arylation Polymerization (DArP), which involved direct carbon-hydrogen (C-H) metalation, has emerged as a reliable alternative to the traditional polycondensations. It allows direct couplings of aryl halides with nonpreactivated arenes, as shown in **Figure 2**, thereby reducing the synthetic steps and, most importantly, avoiding costly toxic organometallic reagents. DArP, thus, does not produce metal-containing toxic waste. Also, the purification step becomes easier as difficult-to-remove byproducts have been minimized [7 - 8]. Another notable advantage is that DArP can produce comparable or higher yields and molecular weights than conventional couplings [9]. DArP, hence, can potentially be applied to prepare a wide range of conjugated polymers.

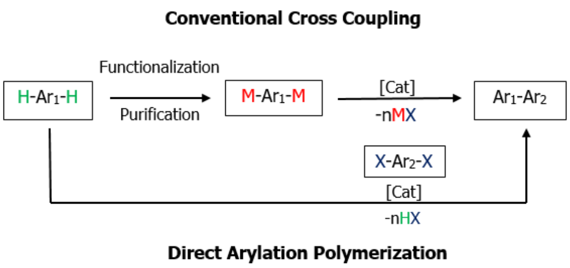


Figure 2. Diagram of conventional cross-coupling (CCP) *vs* direct arylation polymerization (DArP).

Direct arylation generally takes place in the presence of transition metal catalysts and inorganic bases. Owing to the selectivity and reactivity problems, a ligand is often employed in this technique. Ligands bind with the catalyst and influence the bond making and breaking processes at the metal centres. It also stabilizes the catalytic intermediates. Phosphine-based ligands, in particular, have been widely used in DArP. Their application has significantly enlarged the substrates scope of direct arylation. Nonetheless, most of the phosphine-based ligands are costly, toxic and air-sensitive [10-11]. A phosphine-free/ligand-free DArP is thus attractive, considering the environmental issues and instability of the catalytic system.

In this regard, a phosphine-free DArP was employed to synthesize an alternating D-A copolymer, denoted as PCbzDTBT, comprising carbazole as the electron donor and benzothiadiazole as the electron acceptor. Both carbazole (Cbz) and benzothiadiazole (BT) are among the most popular building blocks used in D-A conjugated polymers. With strong electron-withdrawing ability due to the nitrogen atom and the two electron-withdrawing imines (C=N), benzothiadiazole (BT) has been considered as one of the effective building blocks for tuning the energy levels [12].

Polymers based on BT moiety mostly exhibited low band gaps and promising performance [13]. To reduce steric hindrance between donor and acceptor units, π-spacers were introduced to the polymer backbone. Incorporating conjugated spacers renders the copolymer a more planar structure, which improves the charge transport and absorption properties of the polymer. A π-spacer can also influence the optical, electrochemical, and photovoltaic properties of polymers [14].

In this work, a unique D-A copolymer, poly(9,9-didodecylfluorene-alt-thieno[3,2-b]thiophene), **P1,** was developed and synthesised via direct arylation polymerization. The material was then examined to see how this acceptor or π-linker affected the optical band gap of 9,9-didodecyl-2,7-dibromofluorene and whether it could be used as an active layer in PSCs.

METHODS

Materials

Monomers consist of 9,9-didodecyl-2,7-dibromofluorene, and thieno[3,2-b]thiophene was used as received without further purification and purchased from Sigma–Aldrich (Steinheim, Germany). The solvents for the reaction and recrystallize of final products were purchased from Nacalai Tesque (*Kyoto, Japan),* Merck (Darmstadt, Germany), Fluka (Shanghai, China) and BDH (British Drug Houses) (Nichiryo, Japan). The reaction of preparing the polymers was carrying under a nitrogen atmosphere.

Characterization

After the preparation of **P1**, characterization was carried out. The colour and phase of **P1** obtained were observed. Thin-layer chromatography (TLC) was tested by using TLC Silica gel 60 F_{254} (width = 3.7 cm and length = 7.0 cm) as stationary phase and hexane: ethyl acetate (5:1) as mobile phase. A Cole Palmer Ultraviolent lamp box with three wavelengths of 254 nm, 302 nm, and 365 nm was being used to observe the spot of monomers and polymers. For sample analysis, Fourier transforms infrared spectrometer (FT-IR) absorption spectra were acquired using a Germanium ATR attachment on the Agilent Cary 630 FT-IR spectrometer. Without utilizing potassium bromide (KBr) pellets, FT-IR analyses were recorded in the region of 400 to 4000 cm-1. UV-visible absorption spectra were computed by Agilent Cary 60 Double Beam UV-Vis spectrometer. Measurement were conducted under wavelength range between 200 to 600 nm, data interval of 1 nm, the average time of 1.0 s and spectral bandwidth of 2 nm. The absorbance of polymers was identified in a chloroform solution at ambient temperature using rectangle quartz cuvettes (light path length = 10 mm). Nuclear magnetic resonance (NMR) spectra were designated on Bruker 600 MHz NMR spectrometers at 25 ± 8 °C in deuterated chloroform ($CDCl_3$) solution.

Preparation of poly(9,9-didodecylfluorene-*alt*-thieno[3,2-b]thiophene), P1

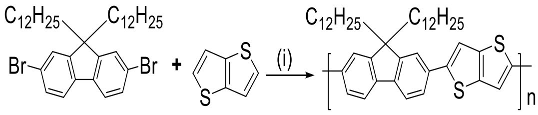
9,9-Didodecyl-2,7-dibromofluorene (260 mg) and thieno[3,2-b]thiophene (55.3 mg), palladium (II) acetate (10.0 mg), pivalic acid (12.1 mg), and anhydrous potassium carbonate (81.7 mg) were stirred in anhydrous dimethylacetamide (3 mL) under inert nitrogen atmosphere. The mixture was degassed before being heated for 72 hours at 110 degrees Celsius. The combination was brought to room temperature after 72 hours of cooling. And thiophene (1 mL) was added. Then, the mixture was degassed and heated again to 110 °C for 3 h. After 3 hours, the liquid was cooled to room temperature and 30 mL of cold methanol was added. To improve precipitation, the solution combination was refrigerated overnight.

The solution mixture was filtered by using membrane filter. The solid collected was dissolved by using chloroform (20 mL). Then, the dissolved solid in chloroform was added dropwise into cold methanol (30 mL). The solids were recovered by filtration through a membrane filter after the solution combination was chilled overnight. The process of dissolving and precipitating was done two more times. The solid obtained was air dried in the fume hood after being repeated two times

RESULTS AND DISCUSSION

Preparation for P1

Polymer synthesis of **P1** was synthesized through modified procedures from Sarjadi and Iraqi [15]. The preparation of polymer **P1** is outlined in **Scheme 1**.



Scheme 1. Preparation of poly (9,9-didodecylfluorene-alt-thieno[3,2-b]thiophene, **P1**. (i) $Pd(OAc)_2$, K_2CO_3, PivOH, DMAc, 100 °C, 72h.

The yield for **P1** was 144.0 mg (57.1%). Colour of **P1** is orange-red. **P1** exist as solid at room temperature, as shown in **Table 1.**

Table 1. The yield, colour and phase of **P1**.

	P1
Yield (mg)	144.0 (57.1%)
Colour	Orange-red
Phase	Solid

Thin Layer Chromatography (TLC)

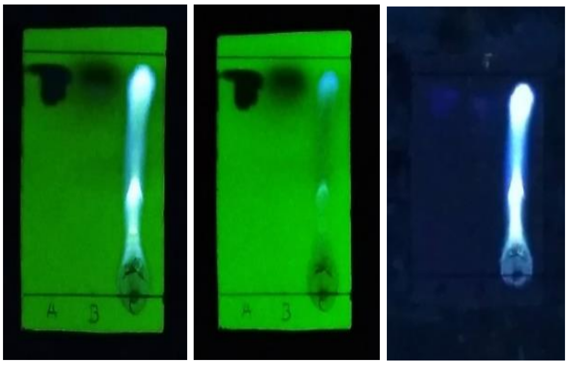


Figure 3. TLC of 9,9-didodecyl-2,7-dibromofluorene, thieno[3,2-b]thiophene and **P1** in UV-box under different wavelength of lights. (a) 254 nm; (b) 302 nm and (c) 365 nm.

TLC was done before polymer purification to check that the reaction was performed with the least amount of unreacted monomers and that the polymer was present. By referring TLC as shown in **Figure 3,** starting from the left point 1 was 9,9-dodecyl-2,7-dibromofluorene, point 2 was thieno[3,2-b]thiophene and point 3 was **P1** under the different wavelength of lights. It was observed that **P1** was present in point 3 as a small dot on the middle of TLC while above the spot was the unreacted monomers.

The spot for polymers was brighter at the 365 nm wavelength of light, according to the TLC of **P1**.

Fourier Transform Infrared Spectrometer (FT-IR)

The FTIR spectrum of **P1** is shown in **Figure 4** with similar patterns to its constituent monomers. Compound **P1** showed strong peaks at 2848.53 cm^{-1} and 2917.50 cm^{-1} for alkyl stretching of methylene groups**.**

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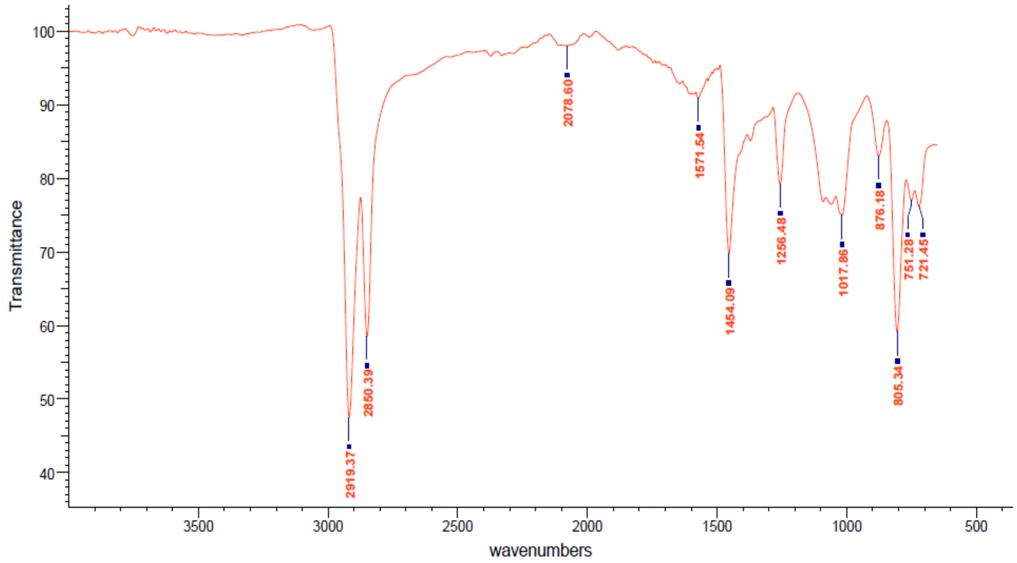

Figure 4. FTIR spectrum of **P1**.

The characteristic overtone at 2108.43 cm^{-1} caused by C-H bending of the aromatic rings is also seen in the spectrum. The characteristic peak at 1454.09 cm^{-1} was assigned for the bending of methylene –CH$_2$, and the peak at 1362.74 cm^{-1}are assigned to bending of methyl –CH$_3$.

Moreover, the medium peak at 1603.23 cm^{-1} and 1688.98 cm^{-1} are assigned to the cyclic C=C stretching. The peaks for aromatic –C=C– stretching can be observed at 1506.29 cm^{-1}. Three sharp peaks at 911.60, 1183.78 and 1338.51 cm^{-1} were observed in thieno[3,2-b]thiophene but not in 9,9-didodecyl-2,7-dibromofluorene has appeared in **P1** at 999.22, 1174.46 and 1362.74 cm^{-1}. Lastly, the peak at 805.34 cm^{-1} was assigned for C-Br bending of the 9,9-didodecyl-2,7-dibromofluorene core system. All the FTIR wavelength data for **P1** are summarized in **Table 2.**

Table 2. Summary FTIR spectrum of **P1**.

Peak	Functional group
805.34 cm^{-1}	C-Br bending
1362.74 cm^{-1}	bending of methyl $-CH_3$
1454.09 cm^{-1}	bending of methylene $-CH_2$ groups
1506.29 cm^{-1}	aromatic –C=C- stretching
1603.23 cm^{-1} and 1688.98 cm^{-1}	cyclic C=C stretching
2108.43 cm^{-1}	C-H bending of an aromatic ring
2848.53 cm^{-1} and 2917.50 cm^{-1}	alkyl stretching of methylene groups

Nuclear Magnetic Resonance (NMR)

Based on the ^{1}H-NMR spectrum in **Figure 5**, **P1** is an unsymmetrical structure with 58 hydrogens. The structure of **P1** was matched with this NMR spectrum.

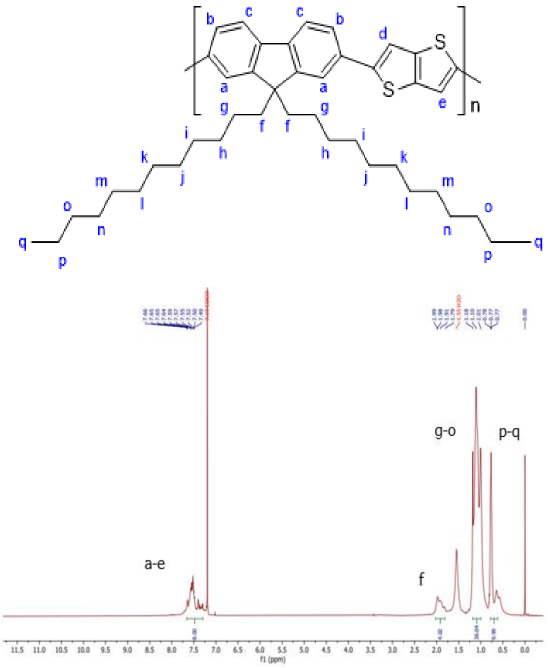

Figure 5. The ^{1}H-NMR (600 MHz, $CDCl_3$) spectrum for **P1.**

Based on the ^{13}C-NMR spectrum in **Figure 6**, **^{13}C-NMR (151 MHz, $CDCl_3$)** δ, ppm: 150.86, 149.35, 139.44, 138.24, 132.49, 129.18, 125.33, 123.84, 119.26, 118.79, 114.30, 54.53, 54.37, 39.34, 30.91, 30.22, 28.69, 28.61, 28.55, 28.52, 28.36, 28.31, 28.18, 22.75, 21.66, 13.10. **P1** is an unsymmetrical structure with 43 carbons and all carbon were assigned as shown in **Figure 6.**

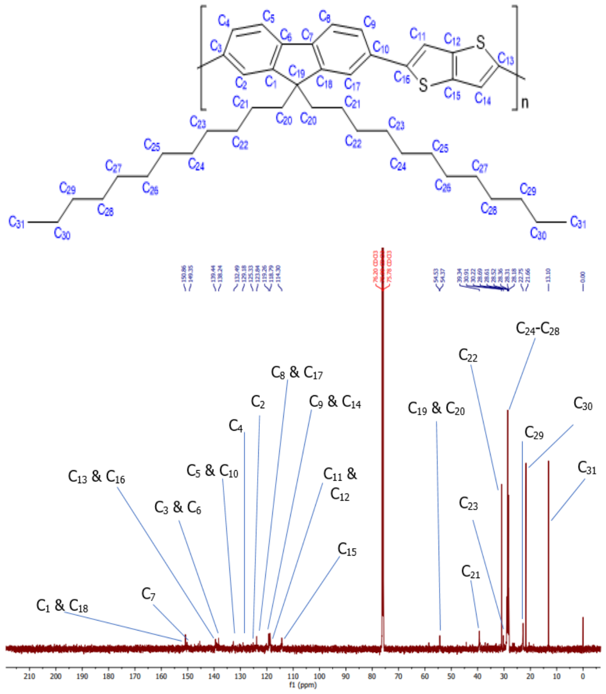

Figure 6. The ^{13}C-NMR(151 MHz, $CDCl_3$) spectrum for **P1.**

Ultraviolet-Visible Spectrometry (UV-Vis)

The UV-Vis absorption spectra of the 9,9-didodecyl-2,7-dibromofluorene, and thieno[3,2-b]thiophene were measured in chloroform. UV-Vis analysis of 9,9-didodecyl-2,7-dibromofluorene, and thieno[3,2-b]thiophene in **Figure 7** showed 9,9-didodecyl-2,7-dibromofluorene has absorption band at λ_{max} = 283 nm, and thieno[3,2-b]thiophene has absorption band at λ_{max} = 271 nm. The monomers absorption spectra were measured to identify its ability to harvest the wavelength at which region of light [16]. By measuring the absorption spectra of constituent monomers to compare the improvement in absorption wavelength of light with the copolymers formed.

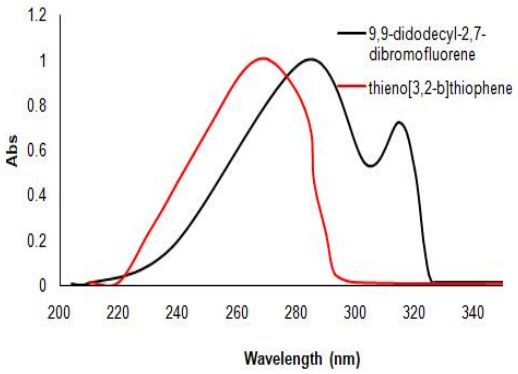

Figure 7. Normalized UV-Vis spectra of 9,9-didodecyl-2,7-dibromofluorene, thieno[3,2-b]thiophene in chloroform.

The UV-Vis absorption spectrum of the **P1** was measured in chloroform. UV-Vis analysis of **P1** in **Figure 8** showed **P1** has two absorption band at λ_{max1} = 242 nm and λ_{max2} = 427 nm.

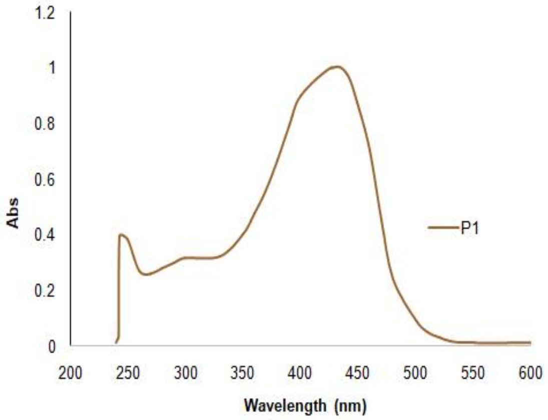

Figure 8. Normalized UV-Vis spectra of **P1** in chloroform.

The optical band gaps of 9,9-didodecyl-2,7-dibromofluorene, thieno[3,2-b]thiophene, and **P1** were calculated from the onset of absorption spectra in chloroform summarized in **Table 3.** The absorption spectrum of monomer 9,9-didodecyl-2,7-dibromofluorene, and thieno[3,2-b]thiophene have an absorption band at λ_{max} located in the ultraviolet region. The optical band gap for 9,9-didodecyl-2,7-dibromofluorene was calculated as a value of E_g = 4.38 eV, and thieno[3,2-b]thiophene is Eg = 4.58 eV. Solar radiation reaches earth consists of ultraviolet, visible and infrared light with different wavelengths. Since 9,9-didodecyl-2,7-dibromofluorene, and thieno[3,2-b]thiophene can only absorb light at an ultraviolent region which is not effective to be applied in PSCs. By forming **P1** able to improve the absorption range and lower the optical band gap.

Table 3. Summary of the bandgap for 9,9-didodecyl-2,7-dibromofluorene, thieno[3,2-b]thiophene, and **P1.**

Sample	λ_{max} (nm)	E_g (eV)
9,9-didodecyl-2,7-dibromofluorene	283	4.38
thieno[3,2-b]thiophene	271	4.58
P1	427	2.91

The absorption spectrum of **P1** have absorption band at λ_{max} located in the ultraviolent region and visible light region. The optical band gap for **P1** has a value of E_g = 2.91 eV. **P1** showed better potential in application of PSCs since it has lower optical band gap. **P1** also able to harvest longer wavelength of light. A lower optical band gap polymer able to has a more promising PCE [15].

When compared to constituent monomers, producing a D-A copolymer results in a reduced optical bandgap. The energy levels of the highest occupied molecular orbital (HOMO) of the donor unit and the lowest unoccupied molecular orbital (LUMO) of the acceptor unit must be appropriately aligned to control the optical band gap for D-A copolymer [13,22]. In **P1**, the donor-acceptor

HOMO and LUMO energy level was well align caused it has increased in λ_{max} when compared to 9,9-didodecyl-2,7-dibromofluorene. Besides, the optical band gap of **P1** also decreases compared to 9,9-didodecyl-2,7-dibromofluorene.

CONCLUSION

Direct arylation polymerization was used to synthesise poly(9,9-didodecylfluorene- alt-thieno[3,2-b]thiophene), **P1,** which is made up of alternating fluorene-based copolymer units. **P1** is comprised of donor and acceptor units that alternated between fluorene and thieno[3,2-b]thiophene. **P1**'s colour and phase were observed. The structure of **P1** was confirmed by using ^{1}H-NMR and ^{13}C-NMR. Functional groups of **P1** was identified by using FTIR. The λ_{max} and range of adsorption of **P1** was identified, and optical band gap were calculated. As an organic compound for use in polymeric solar cells, **P1** looks promising.

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