Imine Coupling Between Thienothiophene and Benzothiadiazole Derivative for Optoelectronic Properties

Hafiz I. Okino, Abdulazeez Yusuf, Ibrahim A. Ibrahim

Abstract—The synthesis of (*E*)-*N*-(benzo[*c*][1,2,5]thiadiazol-4-yl)-1-(3-nonylthieno[3,2-*b*]thiophen-2-yl)methanimine through coupling between 4-amino-2,1,3-benzothiadiazole and 3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde through a series of synthetic routes from functionalisation of the primers of the reactants in a bid to investigate stable Schiff-base benzothiadiazole molecule for opto-electronic applications. A single coupling was successfully achieved from preliminary studies in the 4-amino position of the acceptor molecule and 2-carbaldehyde position of the donor molecule to produce an imine bridge which was however characterised by low stability as it degraded afterwards upon exposure to mild light. Thus, such mechanistic approach suggests unsuitability for obtaining opto-electronic compounds. Para amination was not successful and thus symmetrical D-A-D optoelectronic compound was not achieved.

Index Terms— Opto-electronics, organic solar cells (OSC), organic light emitting diodes (OLED), benzothiadiazole (BT), thienothiophene (TT),
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I. Introduction

The growing demand for renewable sources of energy has not only opened the door to many alternative energies, but furnished a great current of studies in organic-derived opto-electronic compounds which are comparatively cheaper and more accessible. Organic optoelectronics have seen so wide an application in OFET, OSC, OLED that the overwhelming majority of present optoelectronic technologies around us (solar cells, LEDs) are organic based: thanks to its affordability, ease of processibility and functionalisation; achieved through exploiting the delocalisation of pi-electrons in a conjugated system. [1,2, 3].

One of such group of compounds that has found immense relevance and efficacy in organic optoelectronics are thienothiophenes, with emphasis of Thieno[3,2-*b*]thiophene owing to its strong electron donating capacity. Because optoelectronics grossly works on the principle of electron transition within a considerable band gap as suitable for semiconductors (and conductors as well), a highly conjugated electron-rich system as thienothiophenes proves important.

But electron donation is impotent without a complementary electron accepting system. Thus, a conjugation between thienothiophene and benzothiadiazole seeks to achieve such complementarity with conjugation along an imine bridge, for optical and electrical activities: the electron donor increasing the HOMO (valence band) and the electron acceptor reducing the LUMO (conductance band), consequently reducing the band gap for electron transition, and thus limited electrical conduction [4, 5].

The band gap in insulator is very wide with a band gap (E_g) of 10 eV or greater. In conductors, E_g = 0 (or tends towards zero), and have very low resistivity, thus permitting great flow of electrons. A typical semiconductor such as that of silicon crystal has a band gap of 1.1 eV; and in Germanium, 0.7 eV.

The whole objective of organic semiconductors is altering the band gap to one of optimal value. Different organic materials possess varying band gaps depending on the structural modifications and/or doping (Figure 1.1) [6,7].

Amongst organic group of compounds identified with opto-electronic properties, thiophenes have displayed of the finest properties and application in organic semiconductors and conductors due to its highly stabilised aromatic ring courtesy electron-rich and highly mobile sulphur. Due to this, they are often used in *p*-type semiconductors [8]. In contrast, nitrogen-containing building blocks such as benzothiadiazole and quinoxalines are electron poor and withdrawing groups in semiconductor applications. Thus, having greater application in *n*-type semiconductors [9].
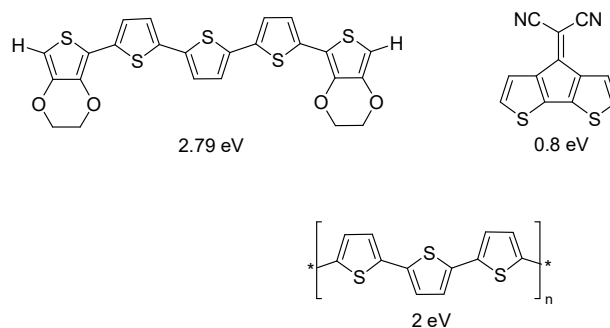

Fig 1.1 Selected semiconducting organic macromolecules with their respective band gaps

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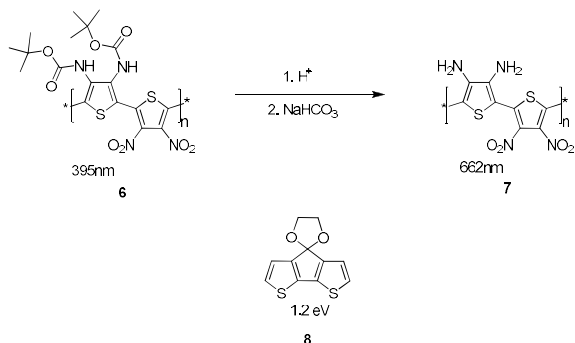****Ibrahim A. Ibrahim**, Chemistry Department, Dialogue College Kaduna, Kaduna, Nigeria

Fig 1.2: Bathochromic shift caused by electron donating substituent and electron withdrawing substituent

In bringing both types of semiconduction together, a push-pull effect is established: thus a Donor-Acceptor (D-A) and Donor-Acceptor-Donor (D-A-D) system. [10]. Further functionalisation, by attaching electron rich substitutents to the donor such as TPA or metoxyTPA has the ability to enhancing charge transfer between the structure of the compound.

D-A-D systems have displayed excellent optoelectronic properties with intrinsic conductivities of $10^{-7} - 10^{-4}$ Scm^{-1} and band gap of 0.79 eV [12].

Imine bridges

Conjugation via imine bridges is challenging its low stability. But with the successful synthesis of self-healing imine-based conjugated polymer by Johannes A. et al [13], it becomes reassuring that with appropriate functionalisation, imine groups may be successful in conjugating donor groups and acceptor group along the electron rich path. This strategy is employed in this research to other to link Thieno[3,2-*b*]thiophene derivative and substituted 2,1,3-benzothiadiazole. [14]

Schiff bases, a product of the condensation of carbonyl and amine groups have had little usage in photovoltaics application as pure organic compounds to the low stability of imine groups of a long period, a concern which concern that proved a challenge at the end of this experimental work. Imines are mildly acidic and protonate to form iminium salt [15]

In this research, an attempt was made to synthesis a D-A and D-A-D system ased on TT and BT through an imine bridge. In the course of achieving this, several synthetics are carried out starting from the two primer thiophene and 2,1,3-benzothiadiazole. The challenge of the imine bridge is tested to observe its extent of stability before proceeding to its optoelectronic properties.
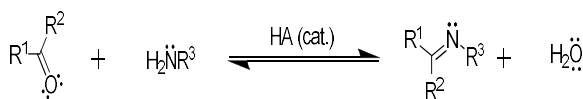

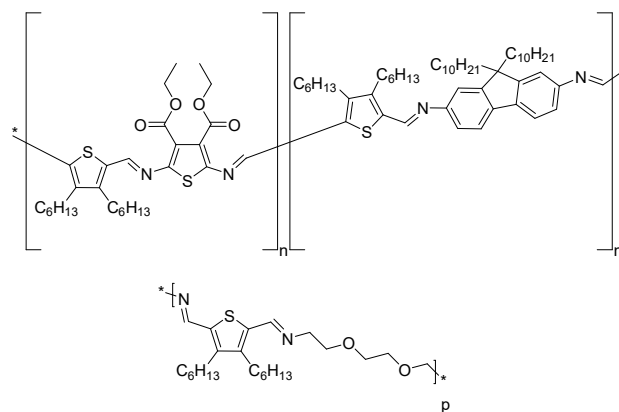Fig 1.3: Imine formation from condensation of aldehyde/ketone with amine

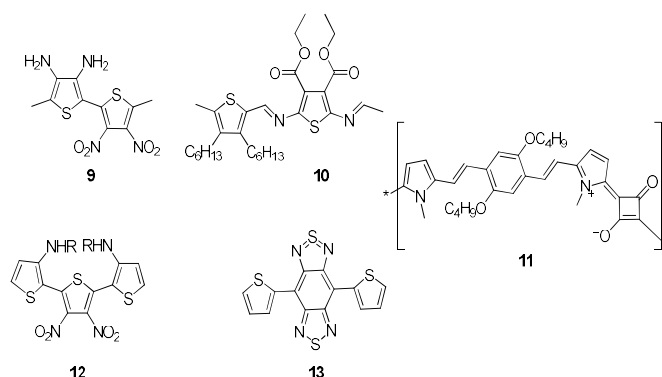**Fig. 1.4:** Self-healing imine-based conjugated polymer [13]

Fig. 1.5: Examples of compounds with low band gap in a D-A and D-A-D system
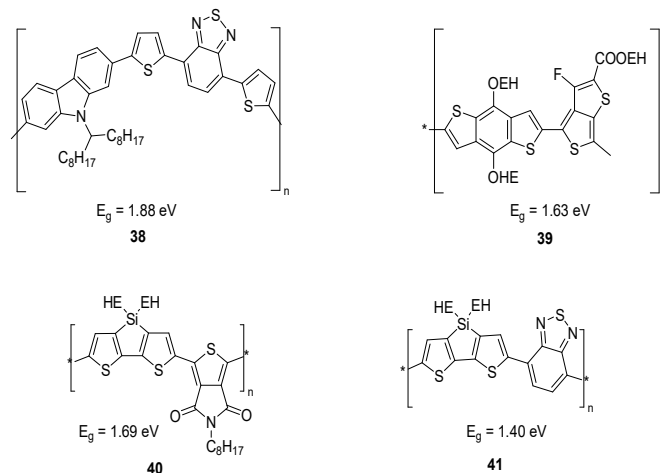

Fig. 1.6: D−A and D−A−D conducting polymers including substituted BT as acceptor group

II. MATERIALS AND METHOD

3-Bromothiophene, 2-undecanone, 2,1,3-benzothiadiazole were obtained from ABCR. *n*-Butyllithium (*n*-BuLi), *tert*-butyllithium (*t*-BuLi), polyphosphoric acid (PPA), ammonium chloride (NH$_4$Cl), *N*-bromosuccinimide (NBS), Zinc, glacial acetic acid (CH$_3$COOH), acetic anhydride (CH$_3$CO)$_2$O, chlorobenzene, potassium hydroxide (KOH), dichloromethane (DCM), *n*-hexane, dimethylformamide (DMF), ethyl acetate (EtOAc), methanol (MeOH), ethanol (EtOH), iron(III)chloride (FeCl$_3$) were supplied by Sigma

Aldrich. Hydrochloric acid (HCl), sulphuric acid (H_2SO_4), nitric acid (HNO_3), chlorosulfonic acid (H_2SO_3Cl), aniline, *N*-formylpiperidine (NFP), diethyl ether (Et_2O), Sulphur (S_8), sodium dithinite $Na_2S_2O_4$, sodium carbonate (Na_2CO_3), sodium bicarbonate ($NaHCO_3$), sodium acetate (CH_3COONa), sodium sulfate (Na_2SO_4) and sodium thiosulfate ($Na_2S_2O_3$) were obtained from Merck.

^{1}H and ^{13}C NMR spectra were recorded on a Varian model NMR (500 MHz). Chemical shifts were reported in ppm relative to tetramethylsilane (TMS). Atoms in the molecule are number and cross matched with their shifts on the spectra.

Synthesized compounds were purified by column chromatography. Merck Silica Gel (0.015-0.040 mesh) was used as the solid adsorbent packed in a glass column. Commercial TLC (Merck TLC Silica Gel 60 F254) was used to control the reaction and determine the eluent ratios for the column chromatography.
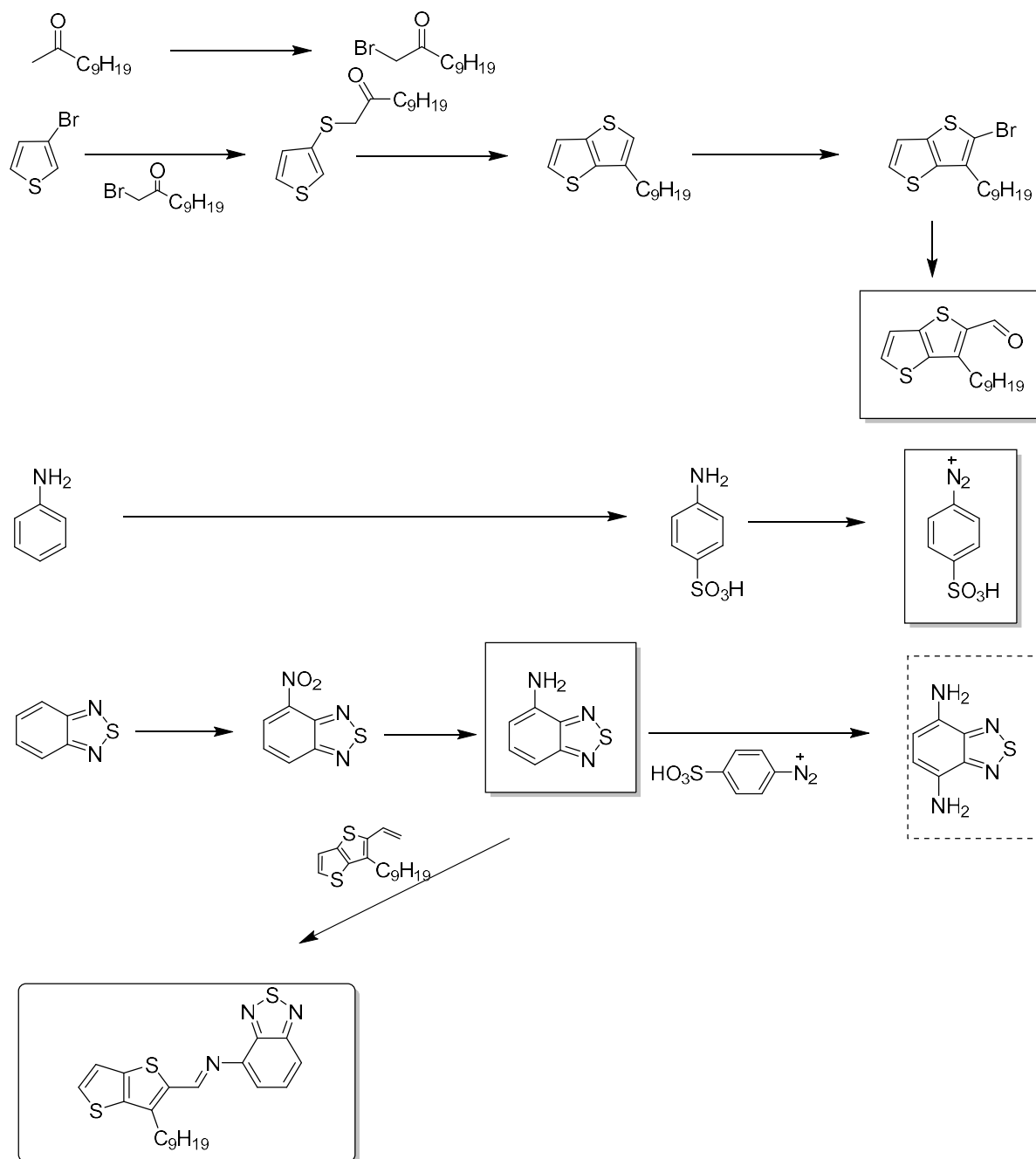
General reaction scheme

III. RESULT

1-bromo-2-undecanone ($C_{11}H_{21}BrO$): To a solution of 2-undecanone (26.00 mL, 0.13 mol) in 220.00 mL MeOH, bromine (21.00 mL, 0.13 mol) was added at -10 °C and then stirred for an hour. It was left for another 1.5 hour stirring at room temperature. Sulphuric acid (120.00 mL, 10.70 *M*) was added into the reaction and left swirling for 24 hours. White

crystals were formed. The supernatant solution was placed in refrigerator for more crystallisation. Residue was collected from filtration using cold water and cold ethanol. To the filtrate n-hexane was added and organic phase was extracted using the separatory funnel. It was allowed to dry yielding more crystals. Combined crystals were dried under vacuum yielding 65% product. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.87 (t, J = 6.0 Hz, 3H, 13-H), 1.26–1.29 (m, 12H, 7–12-H), 1.57–1.63 (quint, J = 6.0 Hz, 2H, 6-H), 2.64 (t, J = 6.0 Hz, 2H, 3-H), 3.88 ppm (s, 2H, 1-H).

1-(thiophe*n*-3-ylthio)-2-undecanone (C$_{15}$H$_{24}$OS$_2$): 3-bromothiophene (2.00 mL, 21.3 mmol) was measured into a three-necked-boiling flask and placed in acetone bath. Under nitrogen, 27 mL distilled Et$_2$O was added into it and mixture is cooled to -78 °C. n-BuLi (9.40 mL, 2.5 M in n-hexane, 23.5 mmol) was added dropwise into the mixture and left stirring for 45 minutes. Sulphur (0.76 g, 23.50 mmol) was measured into the reaction mixture and left stirring for the next 1 hour. Cooling machine was turned off and 1-bromo-2-undecanone (5.86 g, 23.50 mmol) was weighed into the flask. It was left stirring for 1 day under room temperature. Et$_2$O was allowed to evaporate. Extraction was carried out with DCM and NaHCO$_3$; dried with Na$_2$SO$_4$ and purified using silica column chromatography with n-hexane/DCM as eluent. White solid was obtained in 76% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.89 (t, J = 7.0 Hz, 3H, 18-H), 1.26–1.29 (m, 12H, 12–17-H), 1.55–1.60 (m, 2H, 11-H), 2.57 (t, J = 7.4 Hz, 2H, 3-H), 3.58 (s, 2H, 1-H), 7.04 (dd, J = 5.0, 1.3 Hz, 1H, 7-H), 7.22 (dd, J = 3.0, 1.3 Hz, 1H, 5-H), 7.33 ppm (dd, J = 5.0, 3.0 Hz, 1H, 8-H)

3-nonylthieno[3,2-*b*]Thiophene (C$_{15}$H$_{22}$S$_2$): PPA (1.66 g, 16.90 mmol) was weighed into a two-necked boiling flask place in an oil bath. 7.00 mL of chlorobenzene was added and heat was turned on. 1-(thiophe*n*-3-ylthio)-2-undecanone (0.40 g, 1.41 mmol) was dissolved with 3 mL chlorobenzene in a boiling flask. With the aid of a drop pipette, the mixture was transferred into the reaction and heated to 135 °C for 3 days. Chlorobenzene was allowed to evaporate overnight and extraction was carried out with DCM, Na$_2$CO$_3$ and brine. Purification is done using silica column chromatography with hexane/DCM as eluent. Light yellowish viscose oil was obtained in 89% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.92 (t, J = 6.5 Hz, 3H), 1.30–1.41 (m, 12H), 1.79 (quint, J = 7.0 Hz, 2H), 2.76 (t, J = 7.5 Hz, 2H), 7.02 (d, J = 1.2 Hz, 1H, 7-H), 7.27 (d, J = 5.2 Hz, 1H, 2-H), 7.38 ppm (dd, J = 5.2, 1.5 Hz, 1H, 1-H). ^{13}C NMR (500 MHz, CDCl$_3$) δ 14.15, 22.72, 28.64, 29.35, 29.41, 29.44, 29.56, 29.99, 31.93, 119.91, 121.71, 126.54, 134.89, 138.72, 139.96 ppm

2-bromo-3-nonylthieno[3,2-*b*]thiophene (C$_{15}$H$_{21}$BrS$_2$): 3-nonylthieno[3,2-*b*]thiophene (0.35 g, 1.29 mmol) was weighed into a boiling flask wrapped with aluminium foil placed in an ice bath. 10 mL DMF was added and cooled to -10 °C by the addition of NaCl to ice. It was stirred for 5 minutes. NBS (0.25 g, 1.42 mmol) was weighed into the

mixture and left stirring overnight at room temperature. It was extracted with DCM, NaHCO$_3$ and brine. Purification was performed using silica column chromatography with hexane/DCM as eluent. Light brownish oil was obtained with 80% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.28–1.38 (m, 12H), 1.73 (quint, J = 7.2 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 5.3 Hz, 1H, 2-H), 7.40 ppm (d, J = 5.3 Hz, 1H, 1-H).

3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde (C$_{16}$H$_{22}$OS$_2$): 10.00 mL distilled THF was into a three-necked-boiling flask containing 2-bromo-3-nonylthieno[3,2-*b*]thiophene (0.32 g, 1.01 mmol) under nitrogen atmosphere. The mixture was cooled to -78 °C. n-BuLi (0.44 mL 2.5 M in n-hexane, 1.10 mmol) was added dropwise and stirred for 35 minutes. N-formylpiperidine (0.12 mL, 1.01 mmol) was added immediately and the reaction was left for 10 minutes. It was then warmed up to room temperature and left overnight. Extraction was carried out with ethyl acetate and brine; and dried over Na$_2$SO$_4$. Purification was performed using silica column chromatography with hexane/ethyl acetate as eluent. 50% yield was obtained as light oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 0.87 (t, J = 7.0 Hz, 3H), 1.27–1.30 (m, 12H), 1.82 (quint, J = 7.5 Hz, 2H), 3.13 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 5.0 Hz, 1H, 2-H), 7.67 (d, J = 5.0 Hz, 1H, 1-H), 10.1 ppm (s, 1H, 3-H).

4-nitro-2,1,3-benzothiadiazole (C$_6$H$_3$N$_3$O$_2$S): Nitric acid (0.63 mL, 65%, 0.01 mol) and sulphuric acid (1.50 mL, 98%) were measured into a two-necked boiling flask placed in an ice bath. 2,1,3-benzothiadiazole (1.32 g, 10.00 mmol) was added portion-wise while stirring. The reaction was maintained between 0 – 10 °C and left for 3 hours. Extraction was carried out using DCM, Na$_2$CO$_3$ and brine; and dried over Na$_2$SO$_4$. Purification was performed using silica column chromatography with n-hexane/DCM as eluent. Solid yellow crystals were obtained with 71% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.80 (dd, J = 8.8, 7.5 Hz, 1H, 2-H), 8.42 (dd, J = 8.8, 1.0 Hz, 1H, 3-H), 8.60 ppm (dd, J = 7.5, 1.0 Hz, 1H, 1-H). ^{13}C NMR (500 MHz, CDCl$_3$) δ 127.15, 127.62, 128.54 ppm

4-amino-2,1,3-benzothiadiazole (C$_6$H$_5$N$_3$S): Iron powder (0.70 g, 12.50 mmol) was added into stirring 5.00 mL stirring ethanol in a two-necked boiling flask placed on an oil bath. HCl (60.00 μL, 1.25 mmol) was added. The reaction was heated to 65 °C, while stirring for 2 hours; and then cooled to between 55 – 60 °C. 4-nitro-2,1,3-benzothiadiazole (0.45 g, 2.50 mmol) was added portion-wise into the mixture over a period of 30 minutes. It was then stirred at 65 °C for about 3 hours. Reaction was cooled to 40 °C. 5 mL ethanol and 1.00 g of celite were added into the reaction mixture and then filtered over a pad of 1.00 g celite. Residue is further washed with ethanol under reduced pressure. Ethanol is reduced from the mixture under pressure. The filtrate was extracted using

ethyl acetate and Na_2CO_3. Purification was (optionally) performed for extra purity using silica column chromatography with *n*-hexane/ethyl acetate as eluent. Green-yellowish solid was obtained with 76% yield. ^{1}H NMR (500 MHz, CDCl$_3$) δ 4.67 (b. s, 2H, 5-H), 6.64 (dd, *J* = 7.1, 0.8 Hz, 1H, 1-H), 7.36 (dd, *J* = 8.8, 0.8 Hz, 1H, 3-H), 7.41 ppm (dd, *J* = 8.8, 7.1 Hz, 1H, 2-H). ^{13}C NMR (500 MHz, CDCl$_3$) δ, 106.62, 110.09, 131.18, 138.85, 147.79, 155.77 ppm.

Sulfanilic acid (4-aminobenzosulfonic acid) - $C_6H_7NO_3S$: Sulphuric acid (6.10 mL, 108.00 mmol) was measured into a porcelain dish placed on a heating mantle. Aniline (10.00 mL, 107.00 mmol) was added dropwise and carefully into the porcelain. It turned solid for a while. It was heated gradually for 2 hours to 120 ºC and allowed to cool over 30 minutes. It was then heated to 210 ºC for 8 hours. Solid block was pulverised with pestle. 400.00 mL of water was boiled on a heating mantle. The pulverised compound was dissolved in the hot water. 4.00 g of NaOH was added and stirred. Two spatula of activated carbon was added and boiled for few more minutes. The solution was filtered hot. Upon the filtrate, 80.00 mL 30% HCl was added. It was left standing overnight. Fine whitish-grey crystals were filtered from the mixture and dried. Product yield was 51%. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 3.42 (b.s, 2H, 7-H), 7.18 (d, *J* = 8.5 Hz, 2H, 1,5-H), 7.64 ppm (d, *J* = 8.5 Hz, 2H, 2,4-H).

4-sulfobenzenediazonium   ($C_6H_5NO_3S$)   – (*p*-benzenediazonium sulfonate): Na_2CO_3 solution (50.00 mL, 2.5%) was measured into a boiling flask and sulfanilic acid (5.25 g, 30.31 mmol) was added into it while swirling. It was boiled until complete dissolution. Thereafter, the solution was cooled to room temperature. $NaNO_2$ (1.85 g, 26.81 mmol) changed the colour reddish-orange.. HCl was prepared by adding 29 g of ice into 10 mL conc HCl solution. The solution was poured into the ice-containing beaker. White precipitates was formed in few minutes. It was left for 5-10 minutes and then filtered. White residue was dried under vacuum to obtain a yield of 50%. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.10 (d, *J* = 8.7 Hz, 2H, 2,4-H), 8.64 ppm (d, *J* = 8.7 Hz, 2H, 1,5-H).

Imine coupling reaction

4,7-diamino-2,1,3-benzothiadiazole: To a solution of 4-amino-2,1,3-benzothiadiazole (1.00 g, 6.62 mmol) in 0.6 *M* HCl (200 mL) was added portionwise at 0 °C. *p*-benzenediazonium sulfonate was prepared from 1.68 g (9.08 mmol). After stirring for 2.5 h at 0 °C, dark reddish precipitates of the azo dye were filtered and washed with water and acetone. After drying in vacuum, the well-ground powder was suspended in 3 *M* aqueous NaOH (30 mL). To this solution was added portionwise sodium dithinite, $Na_2S_2O_4$ (2.5 g, 14.4 mmol) at 50 °C, and the mixture was heated at 90 °C for 40 min. After cooling, the mixture was

extracted with diethyl ether. The ethereal layer was washed with saturated aqueous $NaHCO_3$ and brine and then dried over Na_2SO_4. Crude product was seperated by column chromatography (Al_2O_3, $CHCl_3$).

(*E*)-*N*-(benzo[*c*][1,2,5]thiadiazol-4-yl)-1-(3-nonylthieno [3,2-*b*]thiophen-2-yl)methanimine: 4-amino-2,1,3-benzothiadiazole (0.1 g, 0.62 mmol) is added into 10.00 mL Ethanol. 3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde (0.18 g, 0.68 mmol) was subsequently added. The solution was stirred at reflux and monitored by until the latter is consumed completely (after 7 hours). Solution was concentrated under vacuum with mild heat (50 ºC). Extraction was carried out using ethyl acetate and dried over sodium sulphate. It was left to dry to produce a yellowish-orange precipitate. The solid however, decomposed under mild (acidic) condition

IV. DISCUSSION AND CONCLUSION

Synthesis of donor group: The thienothiophene-based donor group was synthesised in other to exploit its electron donating capabilities in conjugation with an effective electron withdrawing group through an imine bridge. In other to achieve this, 3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde was synthesised starting from monoketone addition to 3-bromothiophene, then a three-step synthesis of 3-nonylthieno[3,2-*b*]thiophene involving lithiation, addition of elemental sulphur, and then addition of the 2-undecanone moity, to produce **1-(thiophe*n*-3-ylthio)-2-undecanone.**

Ring closure followed to produce stronger electron-donating 3-nonylthieno[3,2-*b*]thiophene. Bromination at C-2 was carried out, then formylation (substitution of bromine at C-2) to produce 3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde.

Synthesis of withdrawing group: 2,1,3-benzothiadiazole (BT) is a good withdrawing group in and of itself. It was derivatised using amino groups. This is to extend conjugation between donor TT and BT via the conjugated system of imine. In other for second amination of BT to occur at *para*-position, the azo-dye *p*-benzenediazonium sulfonate, is required as a catalyst. The catalyst was synthesised from sulphanilic acid. Sulphanilic acid was synthesised from aniline using different methods; some of which are multi-stepped. However, second amination proved a challenge. For the mono substituent, 4-amino-2,1,3-benzothiadiazole was synthesised first and then amination of the C-4 followed to produced 4-amino--2,1,3-benzothiadiazole.

Coupling: Imine coupling was performed between 4-amino-2,1,3-benzothiadiazole and 3-nonylthieno[3,2-*b*]thiophene-2-carbaldehyde. The reaction produced good precipitate but was soon degraded when placed in a very mild acidic medium (turning dark-brown); before complete characterization.

Synthesising symmetric *para*-diaminated BT is possible albeit challenging. In this research, we have attempted second amino substitution at position C-7 to no success. Consequently, the imine coupling reaction with the already synthesised aldehyde-substituted TT was stalled, but

the vital catalyst *p*-benzenediazonium sulfonate was successfully synthesised.

In addition, a monoimine from TT and BT was obtained but wasn't fully characterised due to its very low stability. This is in agreement with the model that imine-groups for PVC applications are not so efficient in pure organic molecules (contrary to organometallic groups). The observation gives further insight to the expected behaviour of the symmetric imine compound if it is eventually synthesised: i.e., poor stability. By and large, this is a step towards the hopeful synthesis of the desired products which can have other applications. We investigated and tested different methods for their actualisation

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