



Synthesis and Characterization of Benzodithiophene (BDT) Quinoid Compounds as a Potential Compound for *n*-Type Organic Thin-Film Transistors (OTFT)

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Abstract

Two potential compounds as an *n*-Type organic thin-film transistor (OTFT) from benzodithiophene (BDT) derivatives have been synthesized and characterized. BDT was chosen as the core because it has π -conjugated bonds, rigid structures, and planar. Quinoid structure with end-cap (terminal group) in the form of dicyanomethylene is used because it can lower the LUMO value of the compound, and side chains are selected in the form of alkoxy so that two BDT derivatives are obtained namely **BDTQ-6** (hexyloxy) and **BDTQ-10** (decyloxy). Based on the results of TGA, **BDTQ-6** and **BDTQ-10** have decomposition points of 183°C and 203°C, which indicate the compound has excellent thermal stability. From the UV-Vis measurement, the λ_{max} value of the two compounds is 599 nm with optical gap energy ($E_{\text{g}}^{\text{opt}}$) of 1.7 eV. From the DPV measurement, the LUMO value for the two compounds is -4.3 eV, with an energy gap (E_{g}) of 1.69 eV (**BDTQ-6**) and 1.70 eV (**BDTQ-10**). Based on observations of the crystal structure through x-ray diffraction, it was found that the **BDTQ-10** crystal has a "brick type" layer arrangement with a distance between layers of 3.55 Å. With excellent thermal stability and suitable LUMO values and energy gaps, it is expected that **BDTQ-6** and **BDTQ-10** compounds have the potential to be *n*-Type OTFT materials.

1. Introduction

Organic semiconductor compounds have attracted many researchers because of their wide use, such as for solar panels [1], organic field-effect transistor (OFET) [2], dye-sensitized solar cell (DSSC) [3], and so forth. Among these uses, OFET attracts much attention and can be used as an alternative to inorganic materials [4]. This is due to several advantages of organic semiconductors such as lightweight, inexpensive, and can be applied to flexible substrates such as plastic. They can be applied to several things, such as electronic paper, sensors, or radio frequency identification (RFID) [5, 6].

Several ring-shaped compounds with conjugated double bonds have attracted attention in their application as semiconductors, such as pentacene and thiophene [7]. Thiophene is a candidate that has been widely developed to form conjugated cyclic compounds, due to its photoelectrochemical properties and better

stability when compared to pentacene. Not only that, but the crystal structure of thiophene also has a rigid and planar structure. The oligothiophene crystal structure, also known to have interactions between S-S atoms, causes the distance between layers to get shorter, making charged mobility is expected to be better [8].

During its development, p-type OTFT has been developed with significant progress, in contrast to the *n*-Type OTFT. Based on several *n*-Type OTFT from oligothiophene, quinoidal compounds with end-cap in the form of dicyanomethylene groups are quite interesting, because they can produce materials with the lowest unoccupied molecular orbitals (LUMO) [9]. Based on the working principle of the *n*-Type OFET, the flow of electrons will be affected by the energy barrier between LUMO and the work function of the source-drain electrode, so reducing the LUMO energy level is very important [10].

Some researchers have developed an OTFT *n*-Type based on thiophene or heterocyclic ring quinoids with end-cap cyanomethyl groups. Wu *et al.* [11] developed a heterocyclic semiconductor named QFBPBP and obtained mobility (μ) of $4 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ with a LUMO of -4.41 eV . Huang *et al.* [12] succeeded in synthesizing Q-dichloromethane-DPPTT, a pyropyrrole-based dicyofene semiconductor with a LUMO value of -4.5 eV . Vegiraju *et al.* [13] has reported a series of DTTQ with a LUMO value of -4.2 eV and the highest mobility of $0.29 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$.

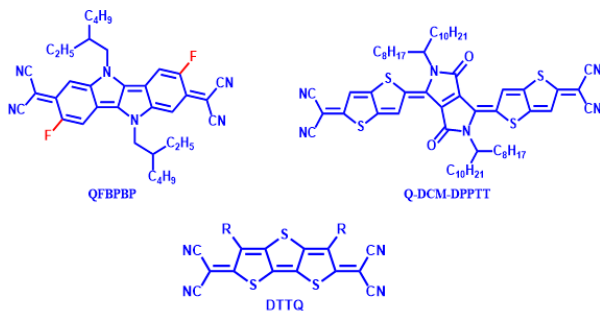


Figure 1. Chemical structure of QFBPBP, Q-dichloromethane-DPPTT, and DTTQ

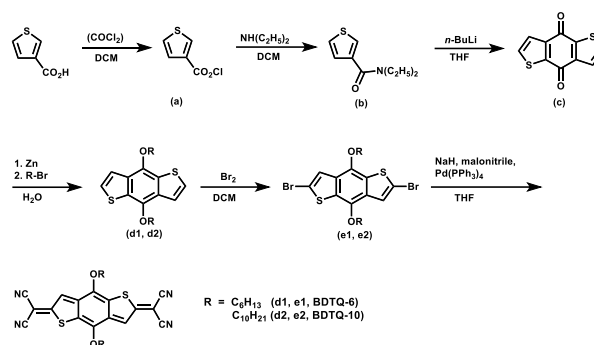
Based on this, in this research, synthesis of potential compounds as *n*-Type thiophene-based organic semiconductors which has a rigid structure and planar conjugation. Fused-thiophene compounds with rigid and planar structures can improve overlapping orbitals between compounds, thereby increasing the efficiency of load transport [13]. The side chain is in the form of alkoxy so that two BDTQ-6 target compounds with an oxadexyl side chain and BDTQ-10 with an oxadexyl side chain are obtained. Both compounds are characterized, both thermal, optical, and electrochemical.

2. Methodology

The materials used in this experiment included, 3-thiophenecarboxylic acid, oxalyl chloride, diethylamine, *n*-butyllithium in hexane (2.5 M), 1-bromodecane, 1-bromohexane, bromine (Br_2), malononitrile, Tetrakis(triphenylphosphine)-palladium(0) ($\text{Pd}(\text{PPh}_3)_4$), water-free tetrahydrofuran (THF) (dry THF), water-free dichloromethane (dry DCM), 325 Mesh zinc powder (Zn), sodium hydroxide, tetrabutylammonium chloride, and sodium hydride dispersed in oil 57–65%. The equipment used included a set of glass and reflux instruments, Hitachi UV-Vis spectrophotometer, ^1H -NMR Bruker Model 300 MHz, and 500MHz, differential pulse voltammetry (DPV) with Pt and Ag/AgCl, thermogravimetric analysis (TGA) with instruments Perkin Elmer TGA-7, and X-Ray Diffraction.

The synthesis of BDTQ-10 and BDTQ-6 compounds starts from the starting material, 3-thiophenecarboxylic acid. In the first stage, 3-thiophenecarboxylic acid is transformed into thiophene-3-carboxyl chloride (b). In the next step, the transformation of compound (b) to *N,N*-diethylthiophene-3-carboxamide (c) is then cyclized to produce benzodithiophene (BDT) (d). Then, the BDT carried out an alkylation reaction on the O atom using

hexyl bromide and desylbromide and continued with bromination and formation of quinoid structures to obtain BDTQ-10 and BDTQ-6 target compounds. Stages of reaction are presented in scheme 1.



Scheme 1. Synthesis of BDTQ-10 and BDTQ-6

2.1. Synthesis of thiophene-3-carboxyl chloride (a)

3-thiophenecarboxylic acid (7.00 g, 54.6 mmol) was put into a 100 mL round bottom flask and dissolved in 40 mL dichloromethane. Then 9.8 mL of oxalyl chloride was slowly added to the flask at 0°C . After that, the mixture was stirred for 24 hours at room temperature. Then, the solvent was evaporated to obtain compound (a) (6.49 g, 39.92% yield) as a pink solid. Compound (a) can be used directly without further purification. ^1H NMR (500 MHz, CDCl_3): δ 8.34 ppm (dd, ^1H , $J = 3.00$), δ 7.574 ppm (dd, ^1H , $J = 6.00$), δ 7.389 ppm (dd, ^1H , $J = 5.00$).

2.2. Synthesis of *N,N*-diethylthiophene-3-carboxamide (b)

Diethylamine (8.1 mL, 78.63 mmol) was added to a 100 mL two-necked round bottom flask containing 30 mL dichloromethane. Then, compound (a) (6.49 g, 39.92 mmol) in 30 mL dichloromethane was added to the diethylamine solution slowly at 0°C . The mixture was stirred for 24 hours at room temperature. After that, the mixture was extracted using dichloromethane/water twice. The organic layer obtained was dried using anhydrous Na_2SO_4 then evaporated to obtain compound (b) in the form of a yellow liquid (6.28g, 85.79% yield). ^1H NMR (500 MHz, CDCl_3): δ 7.469 ppm (dd, ^1H , $J = 3.00$), δ 7.315 ppm (dd, ^1H , $J = 4.50$), δ 7.813 ppm (d, ^1H , $J = 5.00$), δ 3.446 (s, 4H).

2.3. Synthesis of benzo [1,2-b: 4,5-b'] dithiophen-4,8-dion (c)

N,N-diethylthiophene-3-dicarboxylide (b) (3.39 g, 18.89 mmol) was put into 100 mL three-necked round bottom flasks which had been conditioned in an inert atmosphere (N_2). Then, a 40 mL dry tetrahydrofuran solvent was added. After that, 2.5 M *n*-butyllithium (7.53 mL, 17.83 mmol) was slowly added for 30 minutes at 0°C and stirred further for 30 minutes at room temperature. Then the mixture was poured into a beaker filled with ice and stirred for 2 hours. The precipitate formed was filtered and washed using a mixture of methanol and water with a volume ratio of 1: 2 to obtain compound (c) in the form of a green solid (2.8 g, 50% yield). ^1H NMR

(500, CDCl₃): δ 7.683 ppm (d, 2H, J = 4.506), δ 7.648 ppm (d, 2H, J = 5.00).

2.4. Synthesis of 4,8-bis (hexyloxy) benzo [1,2-b: 4,5-b'] dithiophene (d₁)

Benzodithiophene (BDT) (2.2 g, 10 mmol) was suspended in 30 mL of water in a two-neck round bottom flask. Then Zn powder (1.43 g, 22 mmol) was added to the suspension and stirred rapidly, followed by the addition of 6 g NaOH. After that, it was refluxed for 1 hour. After the color of the mixture was turned orange, a quantity of tetraammonium chloride was added to the mixture and 1-bromohexane (4.96 g, 30 mmol) to the mixture and heated for 6 hours. After that, the mixture was poured into cold water and extracted using diethyl ether two times. The obtained organic layer was dried using anhydrous Na₂SO₄ and evaporated. The crude obtained was then purified using a column chromatography method with eluent *n*-hexane: ethyl acetate (19: 1) to obtain pure compound (d₁) (2.3 g, 64% yield). ¹H NMR (500MHz, CDCl₃): δ 7.475 ppm (d, 2H, J = 5.50), δ 7.365 ppm (d, 2H, J = 5.50), δ 4.277 ppm (t, 4H).

2.5. Synthesis of 4,8-bis (decyloxy) benzo [1,2-b: 4,5-b'] dithiophene (d₂)

The procedure used is the same as subsection 2.4 by replacing 1-bromohexane with 1-bromodecane (6.6 g, 30 mmol) and obtaining the pure compound (d₂) (2.8 g, 50% yield). ¹H NMR (500 MHz, CDCl₃): δ 7.473 ppm (d, 2H, J=5.00), δ 7.362 ppm (d, 2H, J=5.00), δ 4.276 ppm (s broad, 4H).

2.6. Synthesis of 2,6-dibromo-4,8-bis (hexyloxy) benzo [1,2-b: 4,5-b'] dithiophene (e₁)

Compound (d₁) (1.02 g, 2.61 mmol) was dissolved in 30 mL dichloromethane into a 100 mL two-neck round bottom flask. Then, bromine (0.83 g, 5.22 mmol) was dissolved in 20 mL dichloromethane and slowly added to the above solution at 0°C and stirred for 7 hours at room temperature. After that, the solvent was evaporated, and crude was purified using the column chromatography method with hexane eluent to obtain (e₁) in the form of a yellowish solid (1.23 g, 86%). ¹H NMR (300 MHz, CDCl₃): δ 7.420 ppm (s, 2H), δ 4.190 ppm (t, 4H).

2.7. Synthesis of 2,6-dibromo-4,8-bis (decyloxy) benzo [1,2-b: 4,5-b'] dithiophene (e₂)

The synthesis was carried out in the same way as subsection 2.6, where (d₂) (1.02 g, 2.03 mmol) and bromine (0.64 g, 4.06 mmol) compounds were obtained (e₂) in the form of yellowish solid (1.22 g, 91%). ¹H NMR (300 MHz, CDCl₃): δ 7.420 ppm (s, 2H), δ 4.190 ppm (t, 4H).

2.8. Synthesis of BDTQ-6

Sodium hydride 60% (117 mg) dispersed in oil was put into a 100 mL three-necked round bottom flask conditioned in an inert atmosphere (N₂). Then 15 mL of dried THF and malononitrile (96 mg, 1.45 mmol) was put into the flask slowly at 0°C, then stirred at room temperature for 30 minutes. After that, compounds e₁ (200 mg, 0.272 mmol) and Pd(PPh₃)₄ (50 mg) were added

to the flask and refluxed. After 48 hours, a solution of Br₂ was added to the mixture. Then, the mixture was extracted using dichloromethane/H₂O three times, and the organic layer obtained was dried with Na₂SO₄, then the solvent was evaporated. The crude obtained was purified using column chromatography with hexane: dichloromethane (1: 1) eluent to obtain BDTQ-6 compounds in the form of green solids (52 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.445 ppm (s, 2H), δ 4.424 ppm (t, 4H).

2.9. Synthesis of BDTQ-10

The same procedure with subsection 2.8 is performed where 60% sodium hydride is dispersed in oil (111 mg), malononitrile (91.99 mg, 1.39 mmol), e₂ compounds (230 mg, 0.348 mmol) and Pd (PPh₃)₄ (200 mg) to obtain BDTQ-10 compounds as green solids (65 mg). ¹H NMR (500 MHz, CDCl₃): δ 7.445 ppm (s, 2H), δ 4.423 ppm (t, 4H).

3. Results and Discussion

3.1. Thermal Properties

TGA analysis results show material decomposition for each material tested. Besides using TGA, BDTQ-6 and BDTQ-10 are also analyzed using the melting point apparatus to determine each material's melting point. TGA results show the composition point at 5% weight loss for BDTQ-6 and BDTQ-10 are 297.52°C and 306.51°C with melting points of 183°C and 203°C, respectively. The thermal properties of the two compounds are summarized in Table 1.

Based on research conducted, thermal stability is an essential trait in developing organic semiconductor compounds to get a useful device. In BDTQ-6 and BDTQ-10, both compounds have excellent thermal stability, as evidenced by their decomposition point above 290°C, as shown in Figure 2. Ogawa *et al.* [14] reported that the anthra [2,3-b] thieno[2,3-d] thiophene (ATT) compound with a thermal decomposition value (5% weight loss) of 290°C, could have mobility amounting to 0.012 cm²V⁻¹s⁻¹. BDTQ-10 has a higher decomposition value because BDTQ-10 has a higher molecular mass due to a longer alkyl chain. In the decomposition process, when heating reaches the decomposition point, the alkyl on both sides of the compound is first released (decomposed). This is confirmed by the percentage of weight reduction in TGA.

Table 1. Thermal properties of BDTQ-6 and BDTQ-10

Compounds	Td (°C)	Tm(°C)
BDTQ-6	297.52	183
BDTQ-10	306.51	203

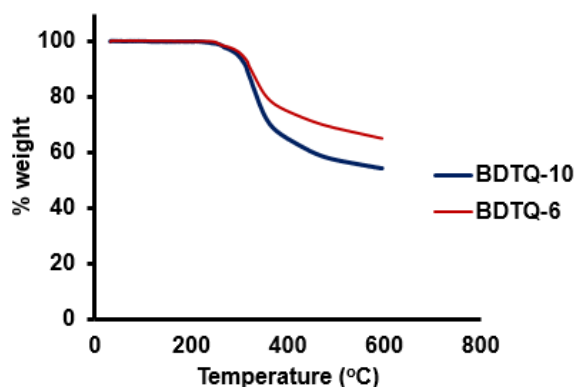


Figure 2. TGA curves

3.2. Optical Properties

In this section, the optical properties of **BDTQ-6** and **BDTQ-10** are discussed by investigating the λ_{max} and λ_{onset} of UV-Vis spectra to obtain the energy gap (E_g^{opt}) of optical data. The results of UV-Vis observations are summarized in table 2. E_g of the two compounds can be measured using the mathematical equation as follows:

$$E_g^{\text{opt}}(\text{eV}) = \frac{1240}{\lambda_{\text{onset}}}$$

Table 2. Optical properties of the BDTQ series

Compounds	λ_{max} (nm)	λ_{onset} (nm)	E_{gap} (eV)
BDTQ-6	599	727	1.71
BDTQ-10	599	724	1.71

The optical properties of the two compounds were analyzed using a UV-Vis spectrophotometer using *o*-dichlorobenzene as a solvent. The UV-Vis graph is presented in Figure 3. Figure 3 shows that the λ_{max} value of the two compounds is 599 nm. This is consistent with the initial predictions that the alkoxy chain will not significantly affect the π -conjugation on the benzodithiophene ring but can be different when BDTQ is measured in its thin-film form. As reported by Vegiraju et.al. [13], the different alkyl chains in the DTTQ series of compounds do not have a significant effect on λ_{max} when measurements are taken on the solution. However, it gives little influence on the results of λ_{max} when formed in thin-film (in this case, it is not performed on BDTQ compounds). This indicates that, in thin-film formation, the side chains (alkyl in DTTQ) will give the different molecular arrangements. The E_g^{opt} of this compound calculated from the edge absorbance is 1.71 eV for **BDTQ-6** and **BDTQ-10**. The optical properties of the two compounds are summarized in table 2.

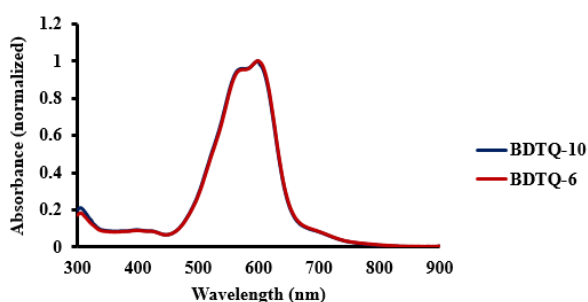


Figure 3. UV-Vis spectra of both compounds

3.3. Electrochemical Properties

In this section, the electrochemical properties of **BDTQ-6** and **BDTQ-10** are discussed. All data were measured using DPV using ferrocene as an internal standard and tetrabutylammonium phosphate solution at 25°C. HOMO and LUMO levels of compounds were calculated based on the oxidation and reduction energy values of **BDTQ-6** and **BDTQ-10**.

Based on DPV data, the HOMO values for **BDTQ-6** and **BDTQ-10** are -6.07 eV and -6.08 eV, respectively, while the LUMO value for both is -4.38 eV. The value, E_g for **BDTQ-6**, is 1.69 eV, while for **BDTQ-10** is 1.70 eV. An illustration of the energy levels of the two compounds is presented in Figure 4. The results of E_g are obtained in accordance with E_g^{opt} data taken from UV-Vis data calculations. This result can be explained by the similarly long benzodithiophene nucleus and the small effect of the length of the alkoxy group on **BDTQ-6** and **BDTQ-10**. Data on the electrochemical properties of the two compounds are summarized in table 3.

Table 3. Electrochemical properties of the BDTQ series

Compounds	E_{red} (eV)	E_{ox} (eV)	LUMO	HOMO	E_g (eV) ^b
BDTQ-6	0.18	1.87	-4.38	-6.07	1.69
BDTQ-10	0.18	1.88	-4.38	-6.08	1.70

The LUMO value obtained is following the requirements to get good material for *n*-Type. Based on Facchetti [15] report, from an energy level perspective, to get an *n*-Type material with good device performance, the LUMO value of material must be in the range of -4.0~-4.3 eV, to obtain a material with good charge transport. Too high LUMO level will produce material that is easily degraded after exposure to ambient air. Conversely, too low LUMO levels will produce materials with strong air resistance (challenging to degrade the surrounding air) but produce devices with difficult turn-offs.

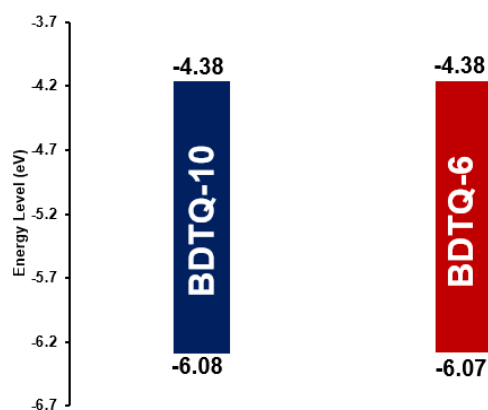


Figure 4. E_g levels of BDTQ-6 and BDTQ-10

3.4. Crystal Structure

In this study, the **BDTQ-10** Crystal structure was obtained from a mixture of methanol and dichloromethane. The results of **BDTQ-10** X-ray diffraction are presented in Figure 5. Figure 5 shows that

on both sides of the nucleus, the CN and BDT nuclei have a C–C bond length of 1.38 Å, which indicates that the bond is a C=C double bond. Besides, **BDTQ-10** also has interactions between molecules in the form of hydrogen bonds between N atoms and H atoms with a bond length of 2.59 Å. The single crystal from **BDTQ-10** has a brick type arrangement with a spacing distance of 3.55 Å and a slipping angle of 85.4°. With a distance between layers of 3.55 Å, it is expected that electrons will flow quickly when applied in utilization as an OTFT, therefore they can get high electron mobility. High mobility can be obtained if the organic material used has a dense crystal structure with a short distance.

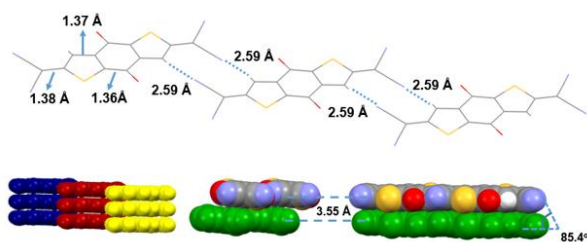


Figure 5. Crystal Structure of **BDTQ-10**

4. Conclusions

Two compounds from the BDTQ series, **BDTQ-6**, and **BDTQ-10**, have been successfully synthesized and characterized. Based on the characterization results, both **BDTQ-6** and **BDTQ-10** have similar thermal, optical, and electrochemical properties. The decomposition points for **BDTQ-6** and **BDTQ-10** compounds are 183°C and 203°C, respectively. The value of λ_{max} of **BDTQ-6** and **BDTQ-10** is 599 nm, with an optical energy gap (E_g^{opt}) of 1.7 eV. The LUMO value on **BDTQ-6** and **BDTQ-10** is -4.38 eV, with an energy gap (E_g) values of 1.69 eV and 1.7 eV. There is no difference in the values of λ_{max} , E_g^{opt} , or E_g due to the same π -conjugation length and a side chain (alkoxy) on the two compounds do not have a significant influence on the HOMO-LUMO level. The LUMO value obtained in this material is suitable for producing good *n*-Type material (-4 eV ~ -4.3 eV). Based on XRD data, it was found that **BDTQ-10** can form crystals with brick type structure, with close spacing between layers. So, from these characteristics, it is expected that both **BDTQ-6** and **BDTQ-10** could potentially be used as *n*-Type OTFT.

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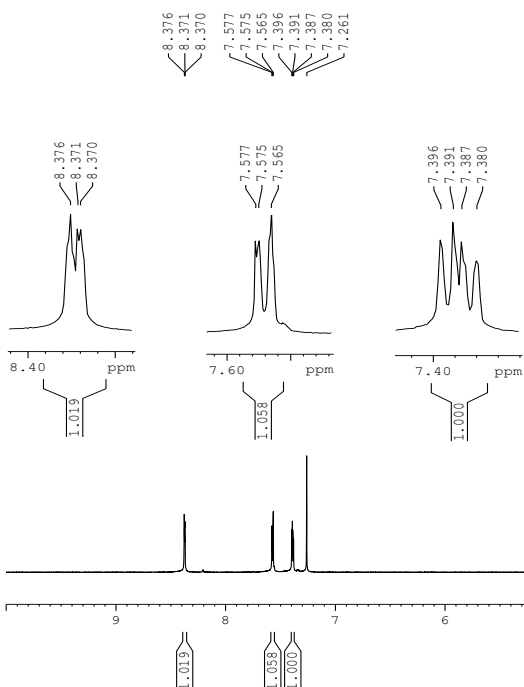
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Supporting Information

1. ¹H NMR of thiophene-3-carbonyl chloride

20180917 thiophene-3-carbonyl chloride



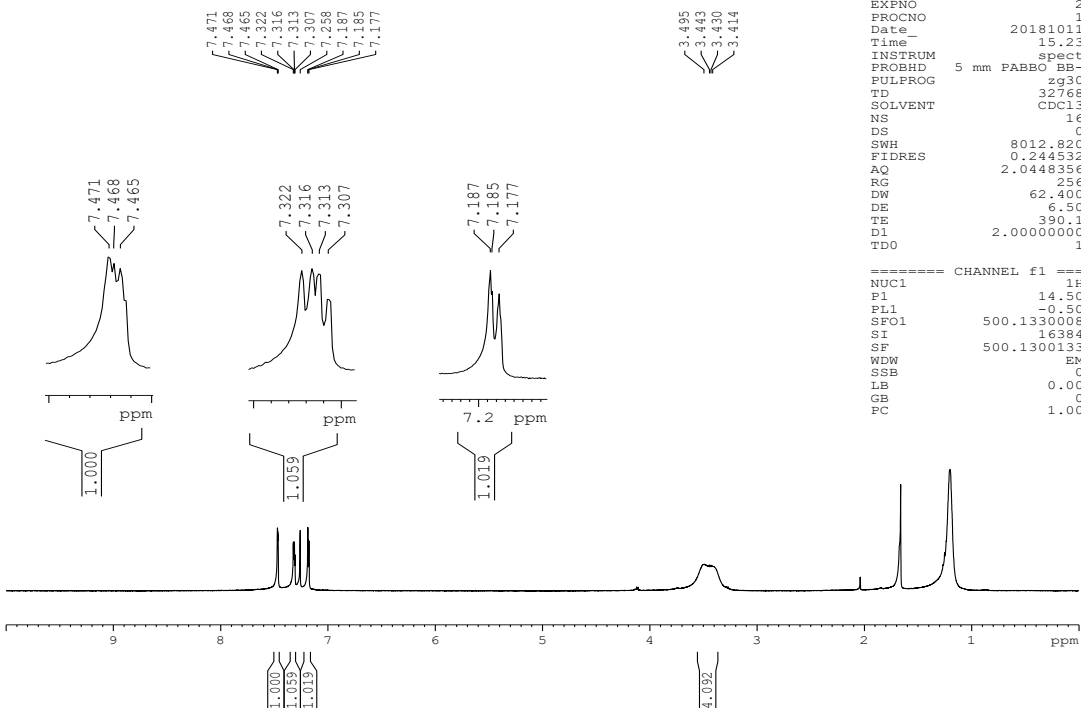
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NAME          20180916
EXPNO         1
PROCNO        1
Date_         20180917
Time          9.42
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PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            0
SWH           8012.820 Hz
FIDRES        0.244532 Hz
AQ            2.0448356 sec
RG            362
DW            62.400 usec
DE            6.50 usec
TE            297.4 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            14.50 usec
PL1           -0.50 dB
SFO1          500.1330008 MHz
SI            16384
SF            500.1300133 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
    
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2. ¹H NMR of *N,N*-diethylthiophene-3-carboxamide (b)

20181011 *N,N*-diethyl-thiophene3-carboxamide



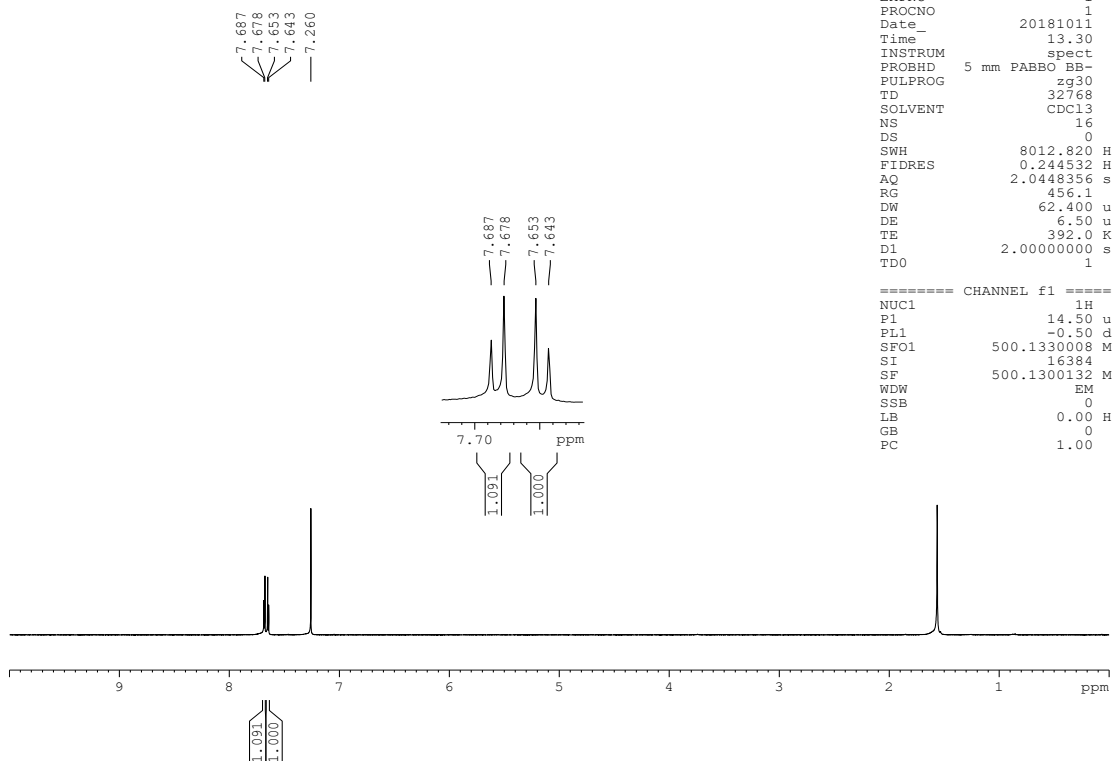
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NAME          20181011
EXPNO         2
PROCNO        1
Date_         20181011
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PULPROG       zg30
TD            32768
SOLVENT       CDCl3
NS            16
DS            0
SWH           8012.820 Hz
FIDRES        0.244532 Hz
AQ            2.0448356 sec
RG            256
DW            62.400 usec
DE            6.50 usec
TE            390.1 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            14.50 usec
PL1           -0.50 dB
SFO1          500.1330008 MHz
SI            16384
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WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
    
```

3. ¹H NMR of Benzo[1,2-b:4,5-b']dithiophene-4,8-dione (c)

20181011 benzo[1,2-b:4,5-b']dithiophene-4,8-dione



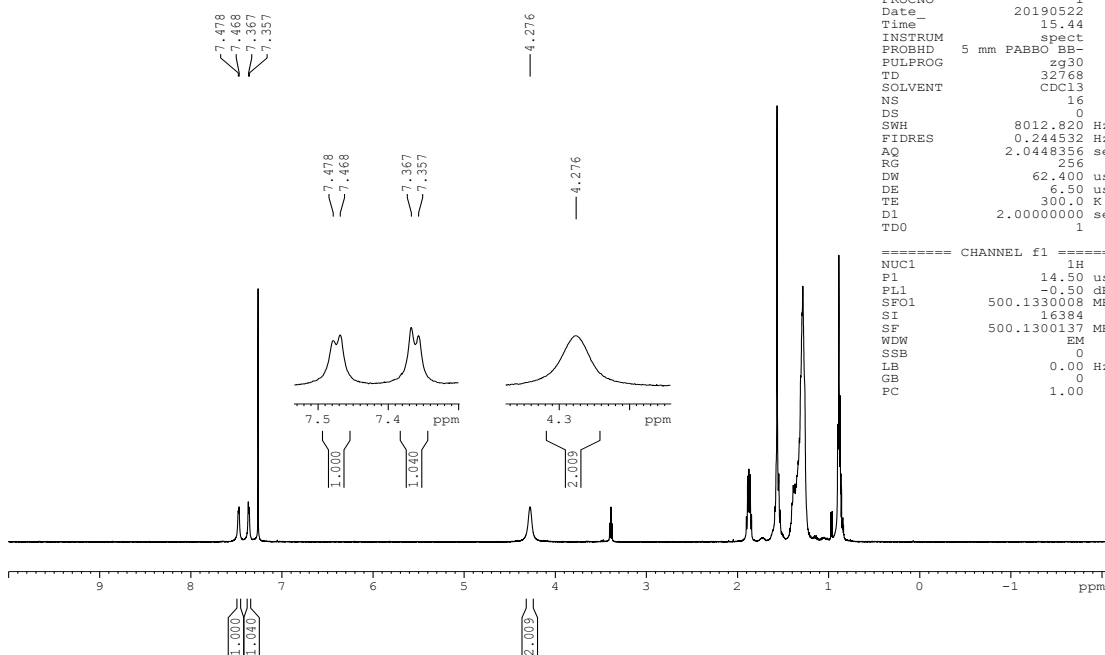
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DS            0
SWH           8012.820 Hz
FIDRES        0.244532 Hz
AQ            2.0448356 sec
RG            456.1
DW            62.400 usec
DE            6.50 usec
TE            392.0 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
NUC1          1H
P1            14.50 usec
PL1           -0.50 dB
SFO1          500.1330008 MHz
SI            16384
SF            500.1300132 MHz
WDW           EM
SSB           0
LB            0.00 Hz
GB            0
PC            1.00
    
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4. ¹H NMR of 4,8-bis (decyloxy) benzo [1,2-b: 4,5-b'] dithiophene (d₂)

BDT-10



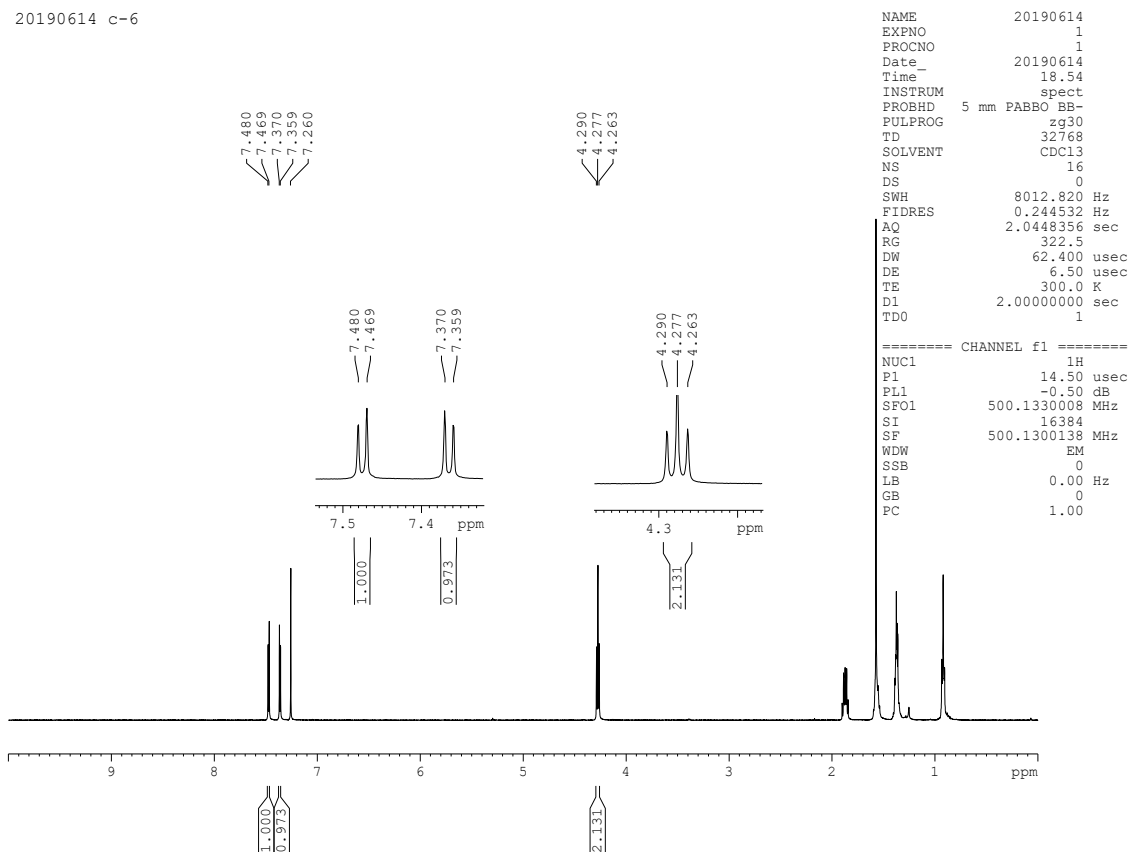
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PROCNO        1
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AQ            2.0448356 sec
RG            256
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DE            6.50 usec
TE            300.0 K
D1            2.00000000 sec
TD0           1

===== CHANNEL f1 =====
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PL1           -0.50 dB
SFO1          500.1330008 MHz
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WDW           EM
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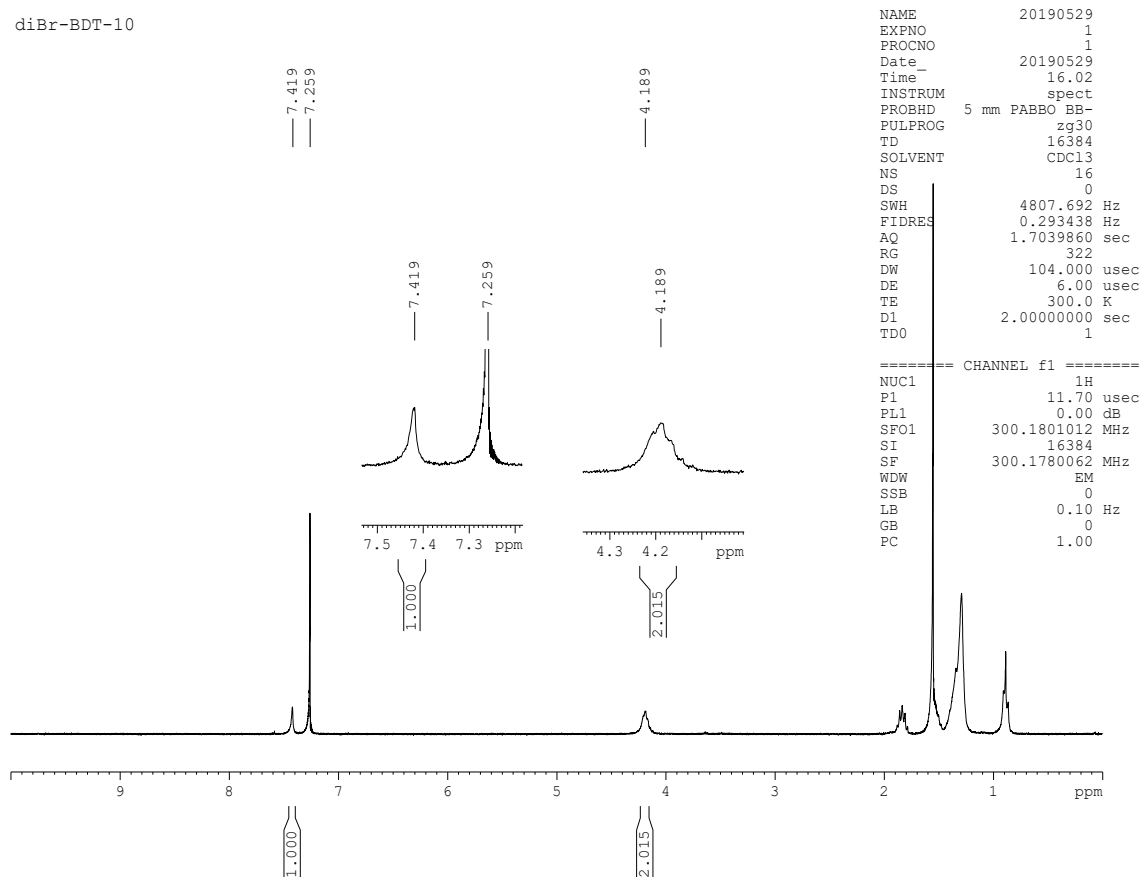

5. ¹H NMR of 4,8-bis (hexyloxy) benzo [1,2-b: 4,5-b'] dithiophene (d₁)

20190614 c-6



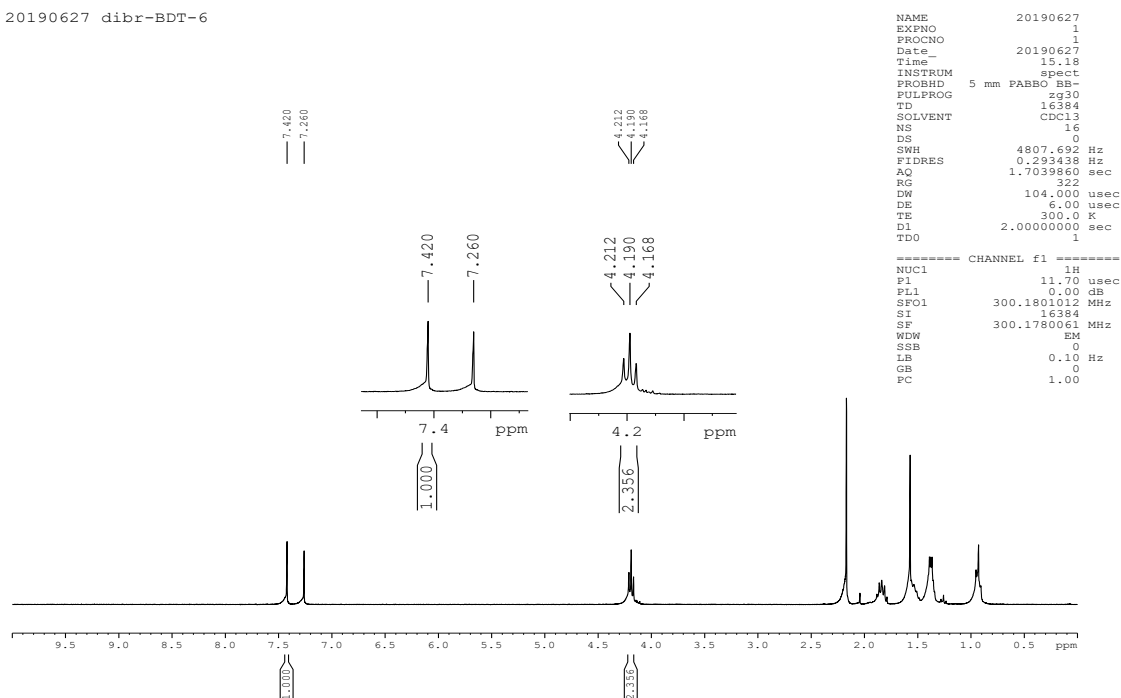
6. ¹H NMR of 2,6-dibromo-4,8-bis (decyloxy) benzo [1,2-b: 4,5-b'] dithiophene (e₂)

diBr-BDT-10



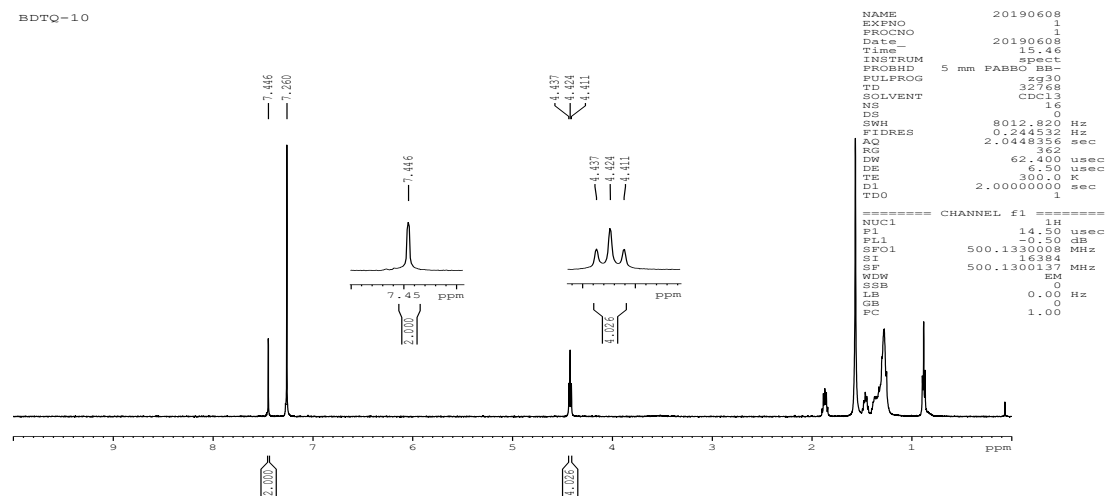
7. ¹H NMR of 2,6-dibromo-4,8-bis (hexyloxy) benzo [1,2-b: 4,5-b'] dithiophene (e₁)

20190627 dibr-BDT-6



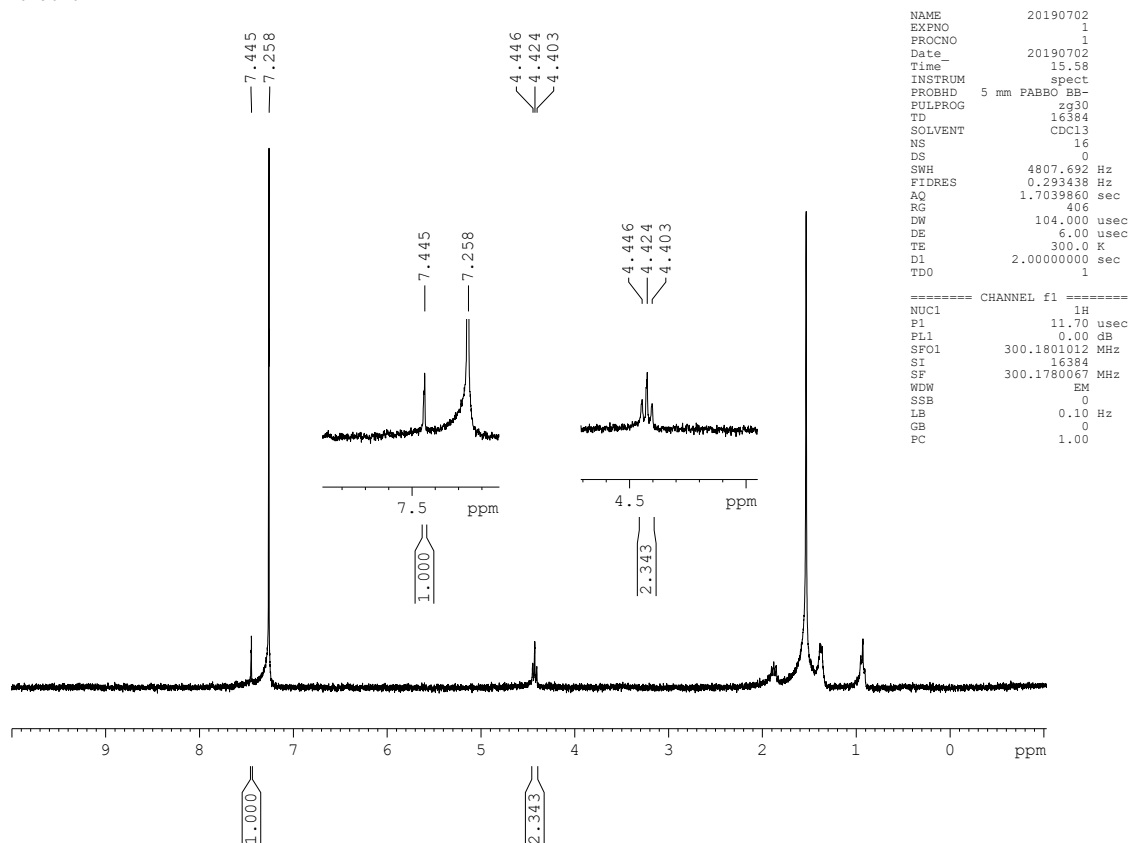
8. ¹H NMR of 2,2'- (4,8-bis (decyloxy) benzo [1,2-b: 4,5-b'] dithiophene-2,6-diylidene) dimalononitrile (BDTQ-10)

BDTQ-10



9. ¹H NMR of 2,2'-(4,8-bis(hexyloxy)benzo [1,2-b:4,5-b']dithiophene-2,6-diylidene) dimalononitrile (BDTQ-6)

20190702



10. Calculation table of HOMO–LUMO through DPV and UV-Vis

Compound	TGA (°C) ^a	DSC (°C)	UV-Vis λ_{max}^b (nm)	E_{gap} (eV)		DPV(eV) ^e	
				DPV ^c	UV-Vis ^d	HOMO	LUMO
BDTQ-10	297.52	185.18	599	1.70	1.71	-6.08	-4.38
BDTQ-6	306.51	-	599	1.69	1.71	-6.07	-4.38

^a5% weight loss, measured by TGA. ^busing *o*-dichlorobenzene as solvent. ^c E_{gap} = LUMO-HOMO. ^dcalculated based on λ_{onset} , $E_{gap} = 1240 / \lambda_{onset}$. ^eall potential reported by DPV with ferrocene as an internal standard in *o*-dichlorobenzene, LUMO = $-(E_{re} + 4.2)$, HOMO = $-(E_{ox} + 4.2)$