Synthesis of Electron-Deficient Discotic Liquid Crystal

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A dissertation submitted for the partial fulfilment of
BS-MS dual degree in Science

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Certificate of Examination

This is to certify that the dissertation titled **"Synthesis of Electron-Deficient Discotic Liquid Crystal"** submitted by **Mr. Rahul Singh Yadav** (Reg. No. MS16008) for the partial fulfilment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Subhabrata Maiti	Dr. Raj Kumar Roy	Dr. Santanu Kumar Pal
		(Supervisor)

Dated: April 30, 2021

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Santanu Kumar Pal at the Indian Institute of Science Education and Research (IISER), Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or Institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me, and all sources listed within have been detailed in the bibliography.

Rahul Singh Yadav

(Candidate)

Dated: April 30, 2021

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Santanu Kumar Pal

(Supervisor)

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Rahul Singh Yadav

List of figures

Abbreviations

LC	Liquid Crystal
DLC	Discotic Liquid Crystal
POM	Polarized optical Microscopy
DSC	Differential Scanning Microscopy
XRD	X-ray Diffraction
TGA	Thermogravimetric Analysis
NMR	Nuclear Magnetic Resonance
AIE	Aggregation-Induced Emission
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
TPE	Tetraphenylethylene
Col	Columnar
DPP	Diketopyrrolopyrrole

Contents

Abstract

Organic semiconductors have gained popularity amongst researchers because of their competitive properties with traditional inorganic semiconductors. The charge carrier mobility is the basic need for an organic compound to be used as an organic semiconductor. Till now, a diketopyrrolopyrrole (DPP) based organic semiconductor has shown the highest charge mobility in a p-type organic semiconductor. The DPP structure can be modified to be used as an n-type semiconductor or as an ambipolar transistor.

In 1970, the DPP core structure was synthesized and published for the first time. After this, DPP was commonly used as a dye in inks and paints for coating purposes. In 1993, the first report regarding conjugated DPP derivatives came. This was the first time when DPP was introduced in the field of organic electronics. In 2008, Nguyen, Janssen, and Winnewisser, along with their respective co-workers, first made DPP-based organic semiconductors for OFETs, OPVs. This work opens the door for making highly efficient organic electronic devices based on the DPP core.

Due to the wide application of DPP in organic materials, we have synthesized novel DPP-based discotic liquid crystal (DLC), which displays liquid crystalline property at room temperature. The purity of the final DLC has been investigated via ^{1}H NMR and ^{13}C NMR. In addition to this, the mesomorphic property has been investigated by Polarizing Optical Microscopy (POM) studies.

In this thesis, we have also synthesized TPE derivatives, which have four phenyl ring with long alkoxy chains directly attached to the TPE core without any linking groups. The purity of the final derivative was confirmed by ^{1}H NMR. But due to the structural property of TPE, it failed to show the liquid crystalline property.

Chapter 1

Introduction

1.1. Phase of matter

Solid, Liquid and Gas are the three important phases of matter but, in between solid and liquid, another phase exists, which is known as liquid crystal. In terms of packing and arrangement of molecules in a lattice, crystalline solids have both positional (molecule have specific site into the lattice) and orientational (each molecule have its molecular axes in fixed direction) order. Molecules in a liquid do not have positional and orientational order. Liquid molecules diffuse randomly throughout sample containers and occupy the shape of the container. In the gas phase, molecules are far apart, and there is no ordering in the molecules.[1]

1.2. What is Liquid Crystal?

Liquid Crystal (LC) is a state of matter which appears like liquid from naked eyes, but when observed in POM, they have a special texture. This special texture appears due to its anisotropic nature. The molecules of all LC phases diffuse as liquid molecules but, they retain a degree of order. In comparison to solid crystals, the amount of order in a LC is very low. Latent heat reveals that most of the order of the crystals are lost as it changes to a liquid crystal phase.[1]

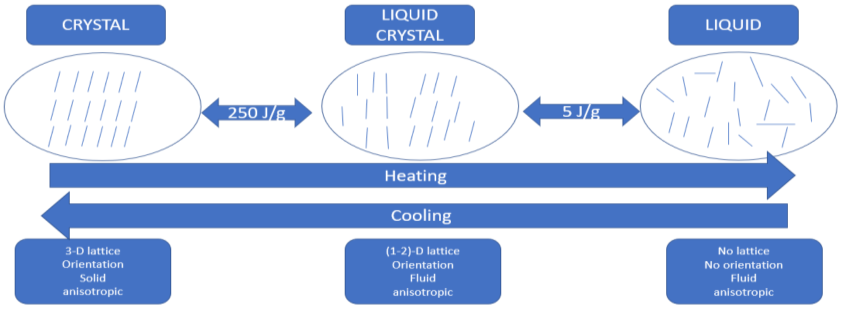

Figure 1 Ordering in a different state of matter (Redrawn from reference [18])

1.3. Types of Liquid Crystals

LC phases are formed by a variety of molecules. All the molecules have one thing in common, i.e. they are anisotropic. LC phase can be either attained by variation in temperature or by changing the solvent in the amphiphilic system. In thermotropic LCs, the LC phase is obtained as a function of the temperature of the material, whereas in the lyotropic LCs, the LC phase is formed in the presence of a solvent.

The rod-shaped molecule is the most common type of thermotropic liquid crystal molecule in which one molecular axis is much longer than the other two axes. They are also called calamitic LCs. The nematic phase is the most common and disordered LC phase of the rod-like molecule.

There are other two phases that are found in calamitic LCs. Those are smectic-A and smectic-C. The smectic phase has a layered structure. If the director is at 90^0 to the layers, then it is called smectic A, and if the director has some other angle than 90^0, then it is called smectic C.[1]

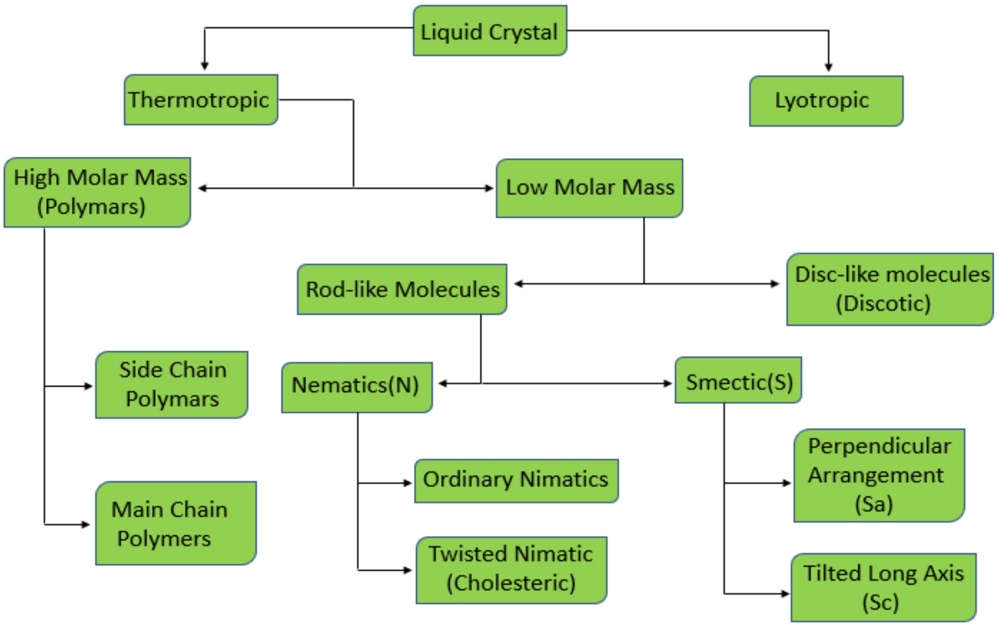

Figure 2 Categorization of LCs (Redrawn from reference [19])

1.4. Discotic Liquid Crystals (DLCs)

In this section, we will discuss DLCs in detail. DLCs were first introduced by Chandrasekhar when he published his work on benzene-hexa-n-alkanoates. In DLCs, one molecular axis is much shorter than the other two axes. The mesomorphic behaviour of DLCs is more sensitive to a slight change in molecular structure. Structures of DLCs consist of a rigid core, peripheral side chains and linking groups.

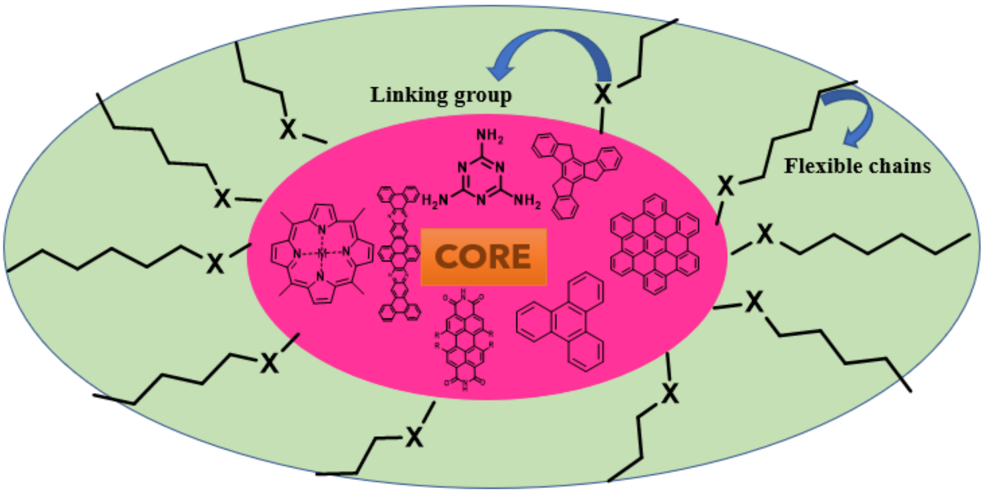

Figure 3 Chemistry of Discotic Liquid Crystals (Redrawn from reference [20])

The central rigid core is typically symmetrical. The peripheral chains are present in numbers that are suitable for the central core to preserve the disc-like shape and help lower the melting points by increasing flexibility. Linking groups increases the side chain length by maintaining the linearity of the core.[2,3,4]

1.5. Type of Discotic Liquid Crystals (DLCs)

Disc-like molecules form a variety of LCs phases. When they self-assemble into columnar form, these one-dimensional columns self-organize into several two-dimensional structures. The column may be in either an ordered or disordered state. Depending on the arrangement of the column, DLCs can organize themselves in the following mesophases: columnar hexagonal mesophase (Col_h), columnar rectangular mesophase (Col_r), columnar oblique phase (Col_b), columnar lamellar (D_L), columnar plastic and columnar tetragonal phase (Col_t).

The shape of the DLCs is the most important factor that controls the self-organization of molecule into liquid crystalline phases. To realize the formation of the nematic phase (N_D) in DLCs, there must be a steric hindrance in the molecule, and terminal chains must be shorter than the size of the central core.[5]

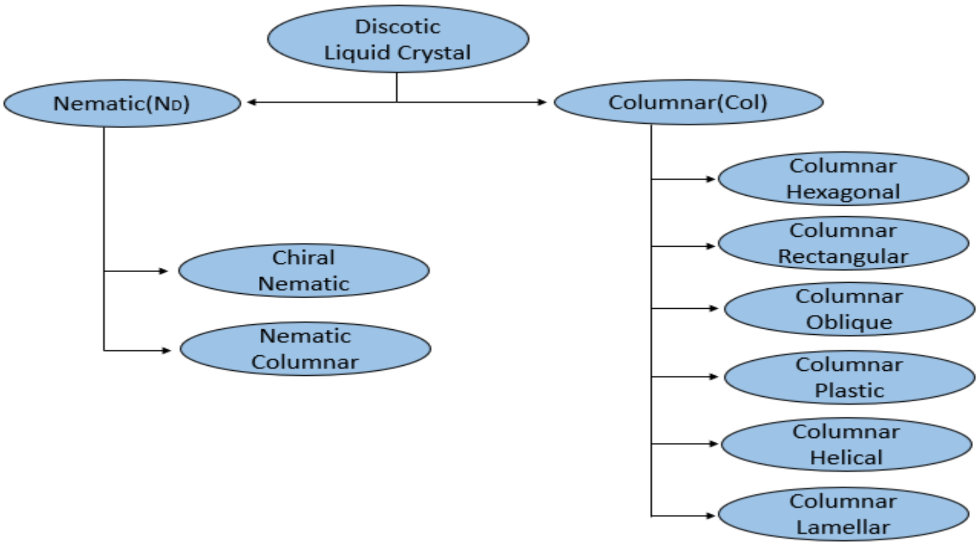

Figure 4 Types of Discotic Liquid Crystals (Redrawn from reference [21])

1.6. Discotic Liquid Crystals in Semiconductor

In 1862, Henry Letheby found polyaniline as partially conducting organic material. Since then, organic semiconductors have been the subject of interest for researchers around the world so that one day they might replace traditional inorganic semiconductors. For any organic material, charge mobility is an essential feature for the application in organic semiconductors and charge mobility depends on molecular self-assembly.

The self-organization of DLCs occurs due to the strong π-π interaction of the core in columnar phases. The intercolumnar core-core separation lies between 0.3-0.38 nm, and the distance between two columns is 2-4 nm (this depends on the length of the side chain). Therefore, the interaction of molecules in a column is much stronger than the interaction of the molecules in two different columns. The columnar phase of DLCs can give the action of charge by hopping from one disc to another disc within a column. Charge transfer in DLCs (columnar phases) are expected to be 1D because conducting core of DLCs is surrounded by an insulating aliphatic chain.[6,7]

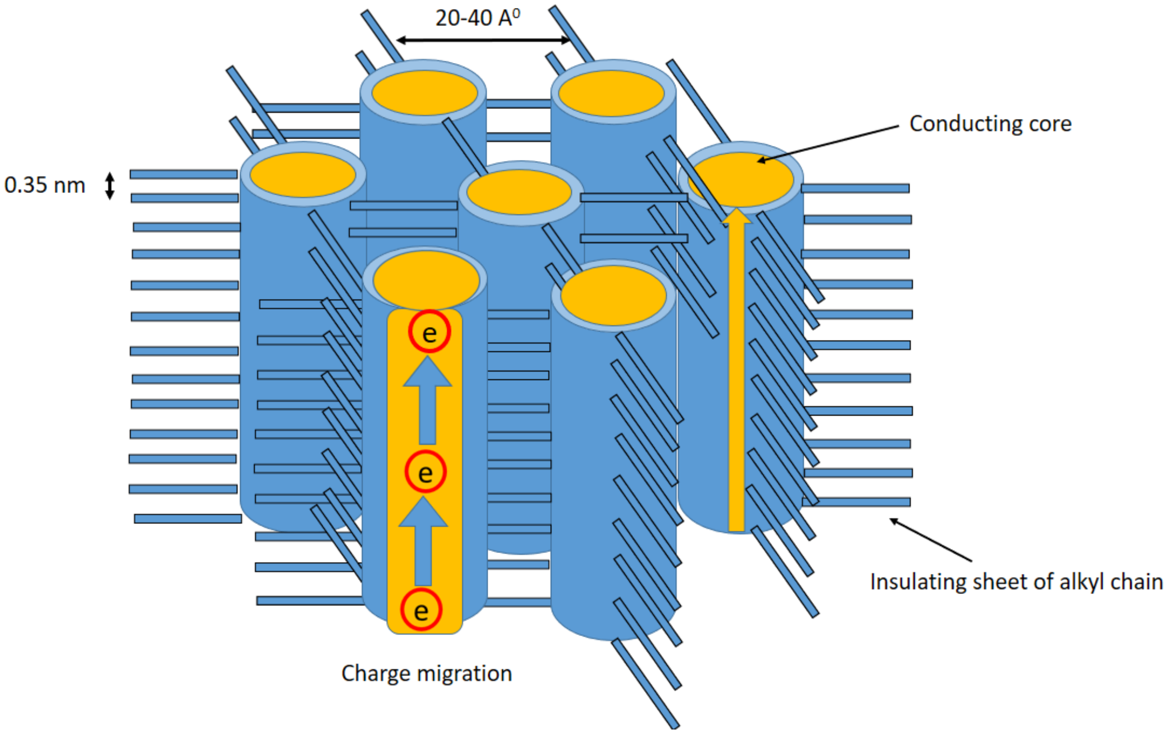

Figure 5 1-D semiconductor columnar mesophase(Redrawn from reference [21])

Chapter 2

Results and Discussions

2.1. Introduction

2.1.1. Tetraphenylethylene (TPE)

Tetraphenylethylene (TPE) core is an excellent solid-state emitter because of poor interaction between the core due to aggregation-induced emission (AIE). The combined effect of AIE and LC has application in OLED and cell-imaging (acidic cellular part). Since it is a tough task to combine both the property (AIE and LC) in a single molecule, there are very few reports on AIE-active LCs. Therefore, we have synthesized AIE active TPE-based derivative by directly attaching four benzene rings having a long chain to the central core (TPE) to investigate the liquid crystalline property.[8,9] The TPE-based derivative was obtained, and purity was confirmed from NMR studies. However, the LC property was not induced in this molecule when POM studies were carried out.

2.2. Synthesize of Tetraphenylethene (TPE) Derivatives

2.2.1. Synthesis Scheme

The detailed synthetic procedures for the final TPE derivative is discussed below:

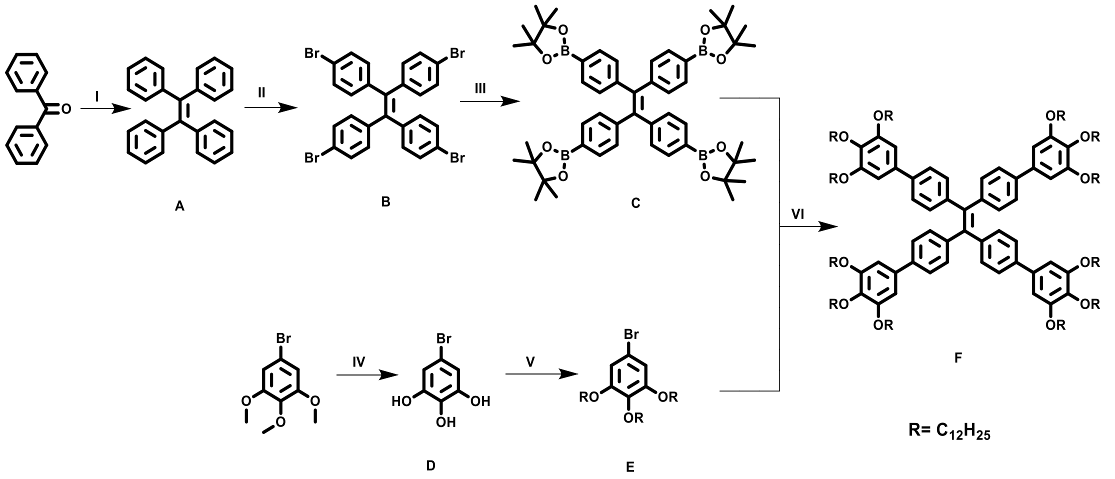

Figure 6 Synthesis of TPE based derivative (F)

(I) Zn, $TiCl_4$ and THF, 12h reflux at 70 °C; (II) Br_2, DCM, RT; (III) B_2Pin_2, Pd(II), KOAc and Dry Dioxane, 16h, 110 °C; (IV) BBr_3, Dry DCM, -78 °C, 12h; (V) R-Br, KI, K_2CO_3, DMF, 30h, reflux at 110 °C; (VI) $Pd(PPh_3)_4$, K_2CO_3, Dioxane and Water (1:5), 48h, reflux at 70 °C.

2.2.2. Experimental Procedure

2.2.3. Synthesis of Tetraphenylethylene. (A)

The Synthesis of compound **A** has been reported elsewhere.[10] Tetraphenylethene core was synthesized by McMurry coupling reaction. In 100 mL one neck round-bottomed (RB) flask, 30 mL dried THF was poured, then activated Zn (7.18g, 109.8 mmol) was added under nitrogen condition and stirred at 0 °C for 10 min. In another 100 mL single neck RB, $TiCl_4$ (5 mL, 54 mmol) was diluted with 30 mL dry THF. This diluted $TiCl_4$ was further transferred dropwise in the first RB. The system was brought to 80 °C and stirred for the next 12 hours. After that, the reaction was cooled to 25 °C and neutralize with 10% aqueous K_2CO_3. The extraction was done with ethyl acetate and water. Further, Na_2SO_4 was used to absorb traces of water in the organic layer, and the solvent (ethyl acetate) was removed using rotavapor. The white colour product (**A**) was obtained. This white product (**A**) was seen under a UV lamp of 365 nm, and a blue-green colour fluorescent was observed. This white colour product (**A**) was obtained. Yield = 89%.

2.2.4. Synthesis of 1,1,2,2-tetrakis(4-bromophenyl)ethene. (B)

The Synthesis of compound **B** has been reported elsewhere.[10] In a single neck RB flask, compound **A** (4g, 12.03 mmol) was dissolved in dry DCM (50 mL) using an ice bath. Bromine (3 mL, 57.3 mmol) was injected dropwise attentively. The system was cooled to 25 °C. It was then stirred continuously for 12 hours. The unreacted reactant was neutralized with sodium bisulfate solution and extracted thrice using DCM. The traces of water in dichloromethane was absorbed with Na_2SO_4, and dichloromethane was evaporated with rotavapor. The product was obtained by recrystallization in HPLC hexane. The white colour product (**B**) was obtained. Yield = 85%.

2.2.5. Synthesis of 1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene. (C)

The Synthesis of compound **C** has been reported elsewhere.[11] In 100 mL two neck RB, mixture of 1,1,2,2,-tetrakis(4-bromophenyl)ethane (**B**, 4g, 12.03 mmol) bis-pinacolato diborane (624 mg, 2.4 mmol), Pd(II) (40 mg, 0.048 mmol) was dissolved in dry dioxane (20 mL). The system was stirred for 24 hours at 110.0 °C. After 24 hours, the system was brought to 25 °C and extracted with diethyl ether till the product was obtained in the organic layer. Traces of water in the organic layer were absorbed with Na_2SO_4 and purified using alumina as a stationary phase in column chromatography. White colour pure product (310 mg) was obtained. Yield = 92% .

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 7.53-7.51 (m, 8H), 7.01-7.00 (m, 8H), 1.34 (m, 48H).

2.2.6. Synthesis of 1-Bromo-3,4,5-trihydroxybenzene. (D)

The Synthesis of compound **D** has been reported elsewhere.[12] In a single long neck RB flask, 1-Bromo-3,4,5-trimethoxybenzene (3.0g, 12.10 mmol) was mixed in DCM (25.0 mL), and the RB was kept at -78 °C for 10 min. BBr_3(10.02g, 40.08 mmol) was further added dropwise (by taking care of safety measures). The reaction was then brought to 25 °C slowly and stirred for the next 12 hours at 25 °C. The extraction was done with EtOAc.

The traces of water was absorbed using Na_2SO_4. Ethyl acetate was evaporated using rotavapor. The obtained compound was recrystallized with ethyl acetate/hexane. White colour solid product (**D**) was obtained and was dried in a vacuum pump for usage in the next step without any purification. Yield = 82%.

2.2.7. Synthesis of 1-Bromo-3,4,5-tridodecyloxybenzene. (E)

The Synthesis of compound **E** has been reported elsewhere.[12] In a 100 mL two-neck RB flask, dry DMF (30mL) was purged with nitrogen for 20 minutes, and 1-bromo-3,4,5-trihydroxybenzene (**D**, 1g, 4.90 mmol) was dissolved. K_2CO_3 (4.5g, 28.40 mmol) was mixed after 10 min. 1-bromododecane (4.02g, 16.20 mmol) was added dropwise, and a pinch of KI was also added. The system was stirred continuously for 30 hours at 115 °C. It was then cooled to room temperature and later extracted using diethyl ether and water. The traces of water were absorbed using Na_2SO_4, and the solvent (ether) was then removed by rotavapor. The compound obtained was refined using column chromatography, and a white colour product (**E**) was obtained. Yield = 85%.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 6.68 (d, 2H), 3.96-3.90 (m, 6H), 1.82-1.73 (m, 6H), 1.59 (m, 6H), 1.28 (m, 48H), 0.91-0.88 (m, 9H).

2.2.8. Synthesis of 1,1,2,2-tetrakis(3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-4-yl)ethene. (F)

In single neck 100 mL RB flask, 1-Bromo-3,4,5-tridodecyloxybenzene (**E**, 3.5g, 4.9 mmol), K_2CO_3 (690 mg, 5 mmol), tetraphenylethylene boronate ester (**C**, 520 mg, 0.62 mmol) and $Pd(PPh_3)_4$ (187 mg, 0.16 mmol) was taken. In another two neck RB flask, 30 mL dioxane and water mixture was taken in a 5:1 ratio, and the freeze pump was used three-time using liquid nitrogen to remove traces of oxygen. After the usage of freeze pump, the solvent was poured in a single neck RB, and the compounds were dissolved and stirred for 48 hours at 110 °C. The extraction was done by EtOAc. The traces of water in ethyl acetate were absorbed by Na_2SO_4. The solvent (EtOAc) was evaporated using rotavapor and refined with column chromatography. The final product (TPE derivative, **F**) obtained was pale yellow in colour. Yield = 30%.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 7.37-7.35 (m, 8H), 7.16-7.14 (m, 8H), 6.7 (m, 8H), 4.04-3.98 (m, 24H), 1.80-1.75 (m, 24H), 1.48 (m, 24H), 1.28 (m, 190H), 0.90 (m, 36H).

2.2.9. Diketopyrrolopyrrole (DPP)

Over the past few years, DPP based functional semiconductors have gained a lot of attention among researchers in the field of organic electronics due to the formation of high-performance materials. Electron deficient DPP core has the ability to produce light-harvesting property. Therefore, DPP based materials are promising candidates for photovoltaics and solar cell applications. DPP core has good intermolecular π-π interaction, which provides the charge carrier mobility property in OFETs. The regulation of the HOMO and LUMO energy levels is possible when different monomers are paired with DPP.[12] The hole and electron mobility of p-type and n-type materials have surpassed 10 $cm^2\ V^{-1}\ s^{-1}$ and 1 $cm^2\ V^{-1}\ s^{-1,}$ respectively. By checking these parameters, the ambipolar DPP core has electron-hole mobility up to 1 $cm^2\ V^{-1}\ s^{-1}$. Due to the extraordinary electronic property of DPP, this is the perfect candidate to improve the performance of devices. The structural change of DPP-based organic materials has mainly concentrated on two areas:(i) adding different linking groups at 3 and 6 positions of DPP; ii) modifying the alkyl group attached to the nitrogen atoms.

In this work, we have linked thiophene, which makes the DPP core a "polar bicyclic electron-deficient conjugated unit", and fall into p-type organic semiconductor materials.[13,14,15]

2.3. Synthesize of DPP Based Discotic Liquid Crystals (DLCs)

2.3.1. Synthesis Scheme

The detailed synthetic procedures for all the final compounds have been discussed below:

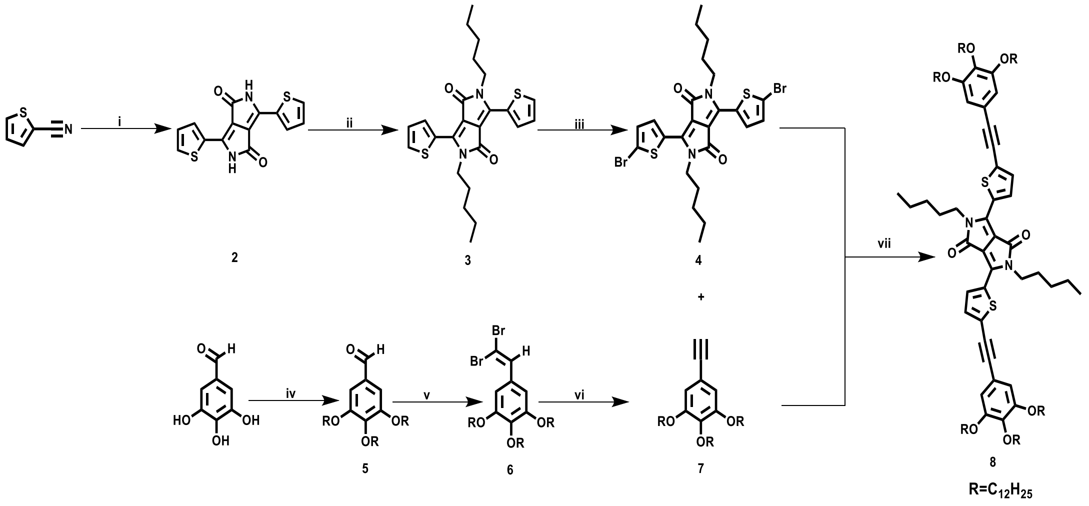

Figure 7 Synthesis of DPP Derivative

(i) Dimethyl succinate, potassium tert-butoxide, tert-butanol, 110 °C, 6h; (ii) RBr, K_2CO_3, DMF, 80 °C, 48h; (iii) NBS, $CHCl_3$, 6h; (iv) RBr, K_2CO_3, DMF, 80 °C, 12h; (v) CBr_4, PPh_3, dry DCM, 5 min; (vi) n-BuLi, dry THF, 24h.

2.3.2. Experimental Procedure

2.3.3. Synthesis of 3,6-Dithiophen-2-yl-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione. (2)

The Synthesis of compound **2** has been reported elsewhere.[16] In a 100 mL two neck RB flask, t-amyl alcohol (20 mL) was purged with nitrogen for 20 min. Potassium tert-butylate (4g, 35.7 mmol) was mixed and 2-thiophenecarbonitrile (3.27g, 30 mmol) was added. The system was stirred for 1.5 hours at 110 °C. In another single neck 50 mL RB, dimethyl succinate (1.46g, 10 mmol) was diluted with t-amyl alcohol (10 mL). The solution from the single neck RB was then transferred to two neck RB dropwise. The ongoing reaction was stirred for another 1 hour at 110 °C. The reaction was then brought to 25 °C, and filtration was done to obtain the crude product. The crude product was then washed with methanol. Dark purple solid product (**2**) was obtained in this step. Yield = 80%.

2.3.4. Synthesis of 2,5-Di(pentan-1-yl)-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione. (3)

The Synthesis of compound **3** has been reported elsewhere.[16] 3,6-Di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**2**) (200 mg, 0.66 mmol) and K_2CO_3 (2.7g, 19.5 mmol,) were mixed in DMF (30 mL) under nitrogen at 110 °C. 1-bromopentane (425.0 mg, 2.979 mmol) was injected dropwise, and a pinch of KI was also added. The reaction was stirred continuously for 36 hours at 115 °C. After 36 hours, the system was kept at 25 °C. The extraction was done with diethyl ether. The traces of water in diethyl ether was removed by Na_2SO_4, and the solvent was evaporated by rotavapor. The pure product was obtained by column chromatography. This product in DCM shows orange fluorescent colour when illuminated under a UV lamp of 365 nm. Yield = 62%.

^1H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.94 (d, 2H), 7.65 (d, 2H), 7.28 (dd, 2H), 4.10 (tt, 2H), 1.77 (dp, 4H), 1.40 (dq, 4H),1.25 (dq, 4H), 0.9 (t, 6H, $-CH_3$).

2.3.5. Synthesis of 3,6-Bis(5-bromothiophen-2-yl)-2,5-di(pentan-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4- dione.(4)

The Synthesis of compound **4** has been reported elsewhere.[16] In 10 mL one neck RB, compound **3** (50 mg, 1.13 mmol) was mixed in dry $CHCl_3$ (5 mL), and NBS (42.2 mg, 2.37 mmol) was then added in dark condition at 0 °C. The system was stirred for 3 hours at 25 °C. The mixture was then extracted using chloroform, and the solvent was removed by rotavapor. Chloroform was dried using Na_2SO_4, and column chromatography was carried out to get the black colour product (**4**). Yield = 49%.

^1H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.70s (d, 2H), 7.24 (d, 2H), 4.0 (dq, 4H), 1.74 (dt, 4H), 1.4 (ddd, 4H), 1.25 (dq, 4H), 0.90 (t, 6H).

2.3.6. Synthesis of 3,4,5-tris(dodecyloxy)benzaldehyde (5).

The Synthesis of compound **5** has been reported elsewhere.[17] Dry DMF was purged in 100 mL two-neck RB with nitrogen for 20-25 minutes. Nextly, 3,4,5- trihydroxy benzaldehyde

(500 mg, 2.41 mmol) and K_2CO_3 (2g, 15.3 mmol) were continuously stirred for approximately 20 minutes. Following this, 1-bromododecane (2.29g, 9.01 mmol) was added along with a pinch of potassium iodide. The reaction was kept for stirring for the next 24 hours at 110 °C. The extraction with diethyl ether was performed. The obtained organic layer was then dried using Na_2SO_4. Diethyl ether was removed using rotavapor, and the product obtained was refined using column chromatography. Yield = 92%.

^1H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 9.83 (s, 1H), 7.08 (s, 2H), 4.07-4.01 (m, 6H), 1.83-1.73 (m, 6H), 1.49-1.45 (m, 6H), 1.30-1.26 (m, 48H), 0.89-0.86 (t, 9H, *J* = 6.84 Hz).

^{13}C NMR (100 MHz, CDCl3, δ in ppm): δ =191.42, 161.33, 153.66, 144.00, 131.58, 107.99, 73.78, 69.38, 64.27, 32.08, 30.49, 29.90, 29.87, 29.84, 29.81, 29.70, 29.64, 29.53, 29.52, 29.41, 29.33, 28.66, 26.22, 26.18, 25.96, 22.84, 14.26.

2.3.7. Synthesis of 5-(2,2-dibromovinyl)-1,2,3-tris(dodecyloxy)benzene (6)

The Synthesis of compound **6** has been reported elsewhere.[17] Compound **5** (1g, 1.52 mmol) was dissolved in 20 mL dry DCM in one neck 100 mL RB. RB was then kept on an ice bath to bring the temperature of RB to 0 °C. CBr_4 (1.01g, 3.03 mmol) was dissolved portion wise for 15 minutes. The solution was left for stirring for another 5min. PPh_3 (1.59g, 6.06 mmol) was further dissolved, and the reaction mixture was stirred at 25 °C for 10 min. TLC was checked to confirm the completion of the reaction by considering compound (**5**) as a reference. The solvent of the reaction mixture was evaporated. Column chromatography was done, and colourless liquid as a pure product was obtained. Yield = 80%.

^1H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 7.37 (s, 1H), 6.76 (s, 2H), 3.98-3.94 (m, 6H), 1.81-1.71 (m, 6H), 1.48-1.31 (m, 6H), 1.34-1.26 (m, 48H), 0.90-0.86 (t, 9H, *J* = 6.84 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): δ =153.01, 148.23, 138.85, 136.95, 130.13, 107.38, 88.20, 73.58, 69.34, 32.08, 30.47, 29.89, 29.85, 29.81, 29.79, 29.74, 29.56, 29.52, 29.49, 26.24, 22.84, 14.26.

2.3.8. Synthesis of 1,2,3-tris(dodecyloxy)-5-ethynylbenzene (7).

The Synthesis of compound **7** has been reported elsewhere.[17] In a single long neck RB flask, dry THF (25 mL) was poured and kept in a -78 °C chiller. Compound **6** (1.4g, 1.91 mmol) was dissolved in dry THF, and n-BuLi (3 mL, 4.8 mmol) was added dropwise while continuously stirring the reaction. The system was elevated to 25 °C slowly and blended for 12 hours. Unreacted n-BuLi was neutralized with NH_4Cl, and extraction was performed in dichloromethane. The obtained DCM was passed through Na_2SO_4. DCM was evaporated using rotavapor. The mixture obtained was refined using column chromatography. The product (**7**) obtained was white. Yield = 63%.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 6.69 (s, 2H), 3.97-3.93 (m, 6H), 2.99 (s, 1H) 1.81-1.73 (m, 6H), 1.45-1.42 (m, 6H), 1.30-1.26 (m, 48H), 0.90-0.86 (t, 9H, *J* = 6.76 Hz).

^{13}C NMR (100 MHz, $CDCl_3$, δ in ppm): δ =153.08, 139.65, 116.54, 110.80, 84.18, 75.89, 73.66, 69.27, 32.09, 30.45, 29.89, 29.85, 29.82, 29.79, 29.74, 29.53, 29.45, 26.24, 26.22, 22.85, 14.27.

2.3.9. Synthesis of 2,5-dipentyl-3,6-bis(5-((3,4,5-tris(dodecyloxy)phenyl)ethynyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.(8).

In 15 mL single neck RB flask, mixture of 123-tris(dodecyloxy)-5-ethynylbenzene (**7**, 300 mg, 0.49 mmol), 3,6-bis(5-bromothiophen-2-yl)-2,5-di(pentan-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**4**, 104 mg, 0.17 mmol), $[Pd(PPh_3)_4]$ (20 mg, 0.017mmol), CuI (9 mg, 0.052 mmol) was taken. In another two-neck RB flask, 15ml toluene was freeze pumped by liquid nitrogen and transferred to single-neck RB by using canula. In the end, 2 ml di-isopropyl amine was introduced to the mixture and stirred continuously for 24 hours at 110 °C. The reaction mixture was brought to 25 °C. Toluene was removed, and extraction was done with EtOAc. Traces of water in ethyl acetate was absorbed using Na_2SO_4. Ethyl acetate was evaporated by rotavapor. The crude product was further refined with column chromatography, and deep blue colour pure product (**8**) was obtained. Yield = 65%.

^{1}H NMR (400 MHz, $CDCl_3$, δ in ppm): δ = 8.94 (d, 2H), 7.3 (d, 2H), 4.0 (dq, 4H), 1.8 (dt, 16H), 1.4 (ddd, 12H), 1.25 (dq, 4H), 0.90 (t, 6H), 6.69 (s, 4H), 3.97-3.93 (m, 12H), 2.99 (s, 1H), 1.81-1.73 (m, 8H), 1.45-1.42 (m, 6H), 1.30-1.26 (m, 96H), 0.90-0.86 (t, 24H).

2.4. Characterization

2.4.1. Polarized Optical Microscopy (POM)

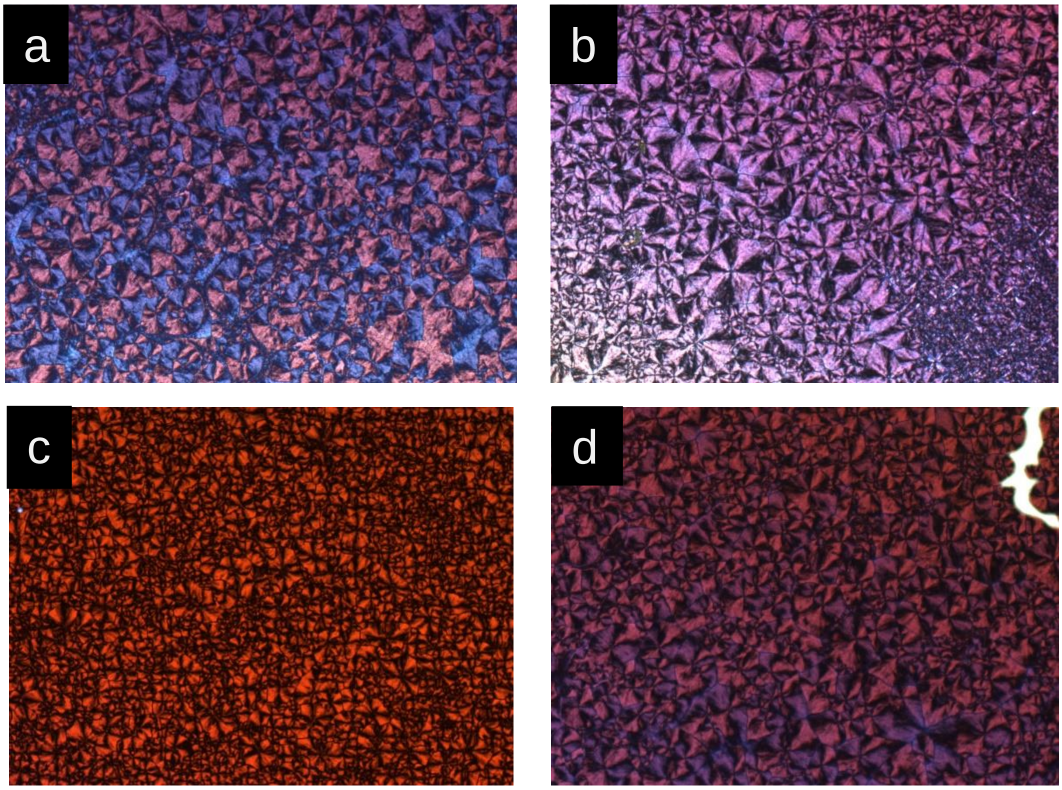

Figure 8 POM image of DPP derivative.

Optical micrographs of DPP derivative : (a) 40 ºC (X200) , (b) 45 ºC (X200), (c) 55 ºC (X100), (d) 60 ºC (X200), (scan rate: 5 ºC /min.).

2.5. Conclusions and Future Outlook

We have tried to synthesize TPE-based discotic liquid crystals. Four phenyl groups directly attached to ethene disrupts the π-π interaction within the core due to their rotational nature, which results in the non-LC property of TPE-based derivative.

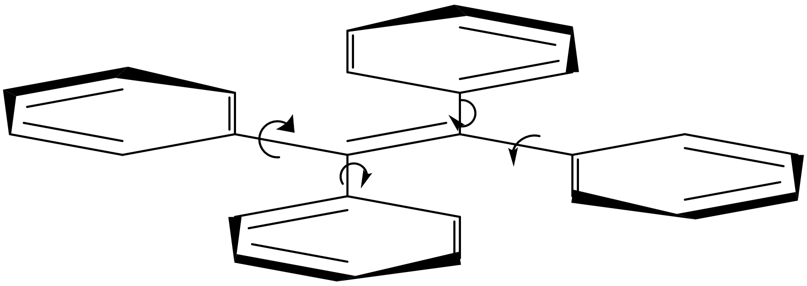

Figure 9 Rotating structure of TPE core (Redrawn from reference [22])

Mesomorphic studies (POM, DSC, XRD) were carried out to confirm the liquid crystalline behaviour. However, the stacking property of this type of compound can be increased by attaching a bithiophene group which could potentially lead to the induction of liquid crystalline behaviour.

However, we got success in synthesizing DPP-based discotic liquid crystal, which has wide application in future generation organic semiconductor. The liquid crystalline behaviour was confirmed by POM texture, showing four brush defects. The LC phase was attained from 62 °C to room temperature in the cooling cycle. Other studies like XRD, DSC, TGA, UV, Electrochemical property, device fabrication will be done in the future.

Appendix

3.1. Nuclear Magnetic Resonance (NMR)

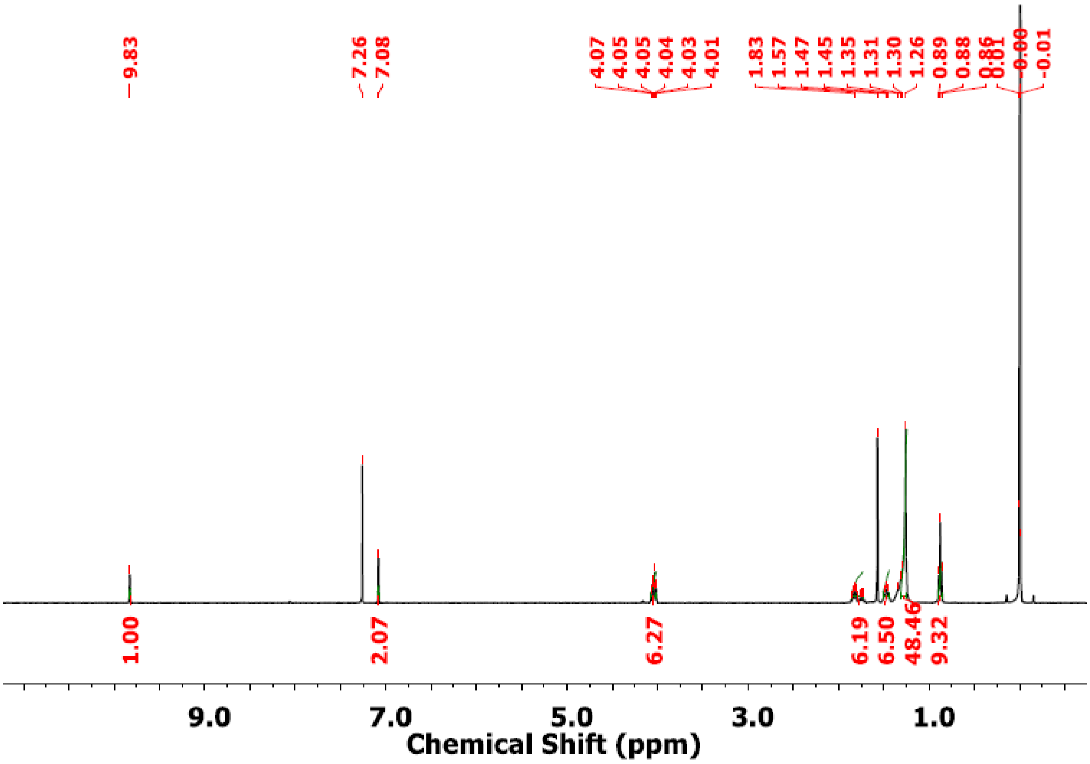

Figure 10 ^{1}H NMR of 3,4,5-tris(dodecyloxy)benzaldehyde (**5**)

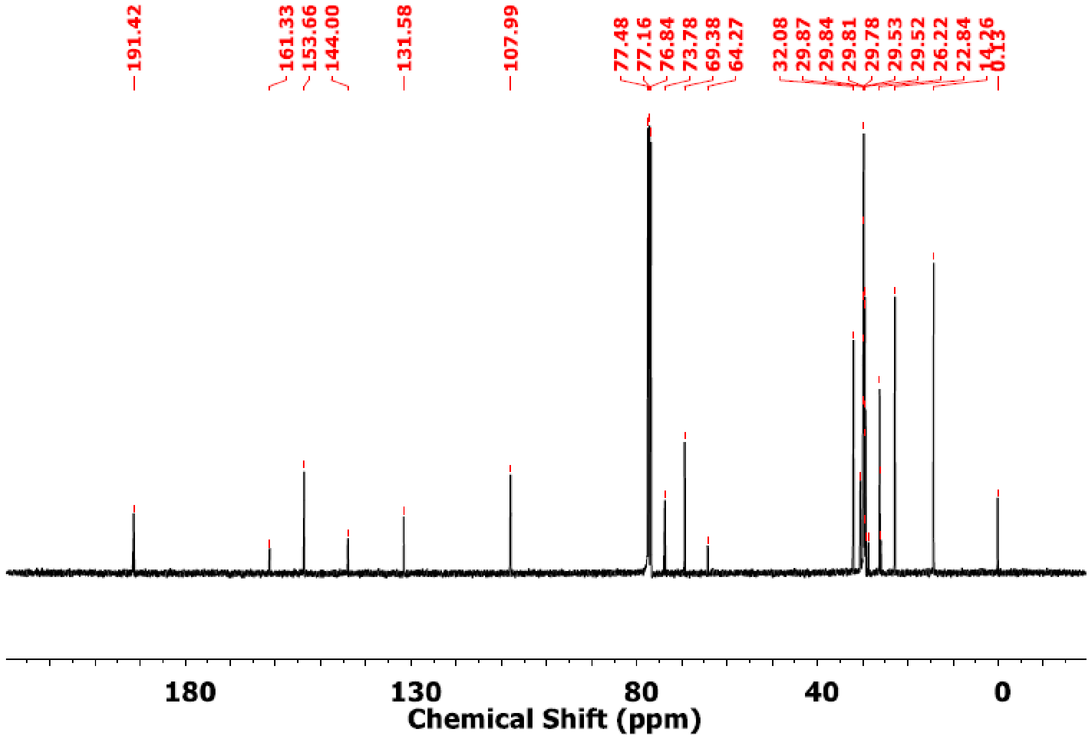

Figure 11 ^{13}C NMR of 3,4,5-tris(dodecyloxy)benzaldehyde (**5**).

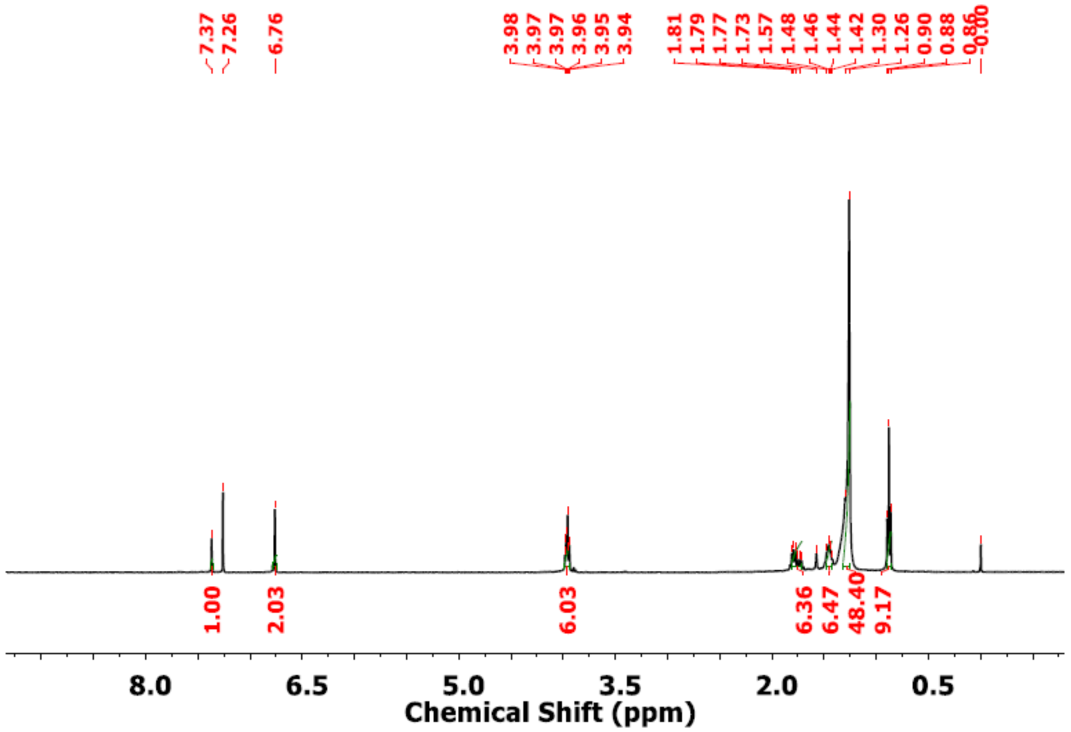

Figure 12 ^{1}H NMR of 5-(2,2-dibromovinyl)-1,2,3-tris(dodecyloxy)benzene (**6**).

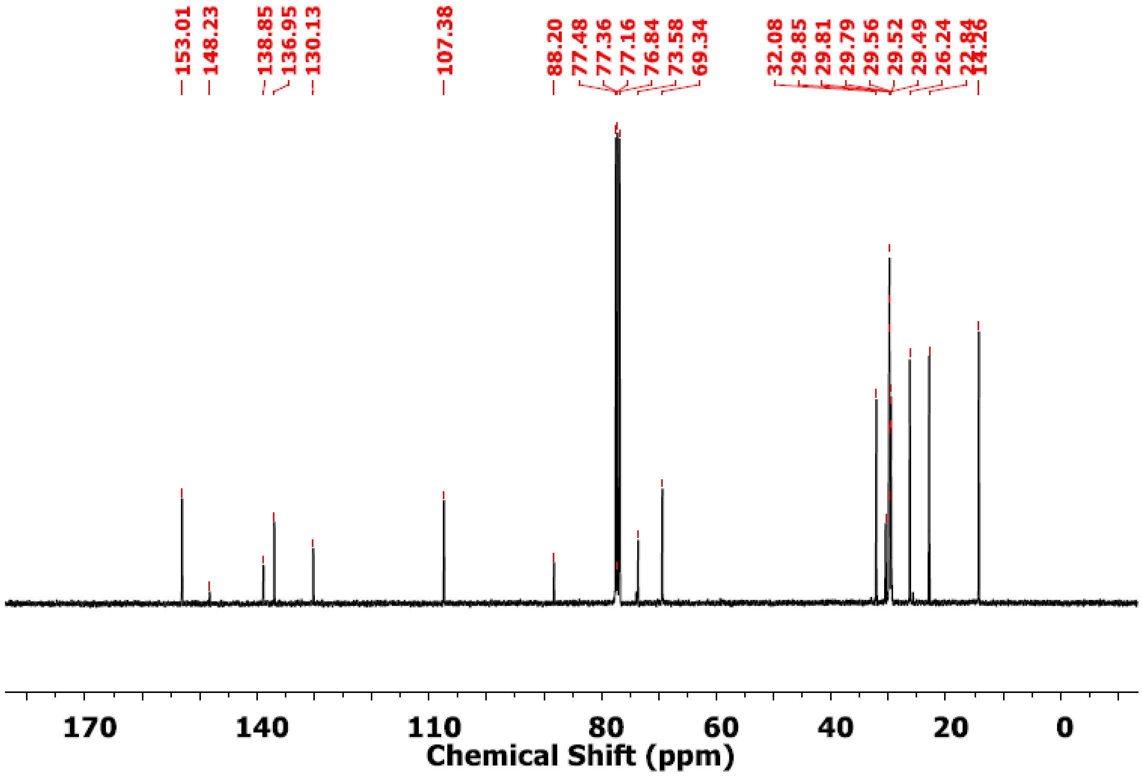

Figure 13 ^{13}C NMR of 5-(2,2-dibromovinyl)-1,2,3-tris(dodecyloxy)benzene (**6**).

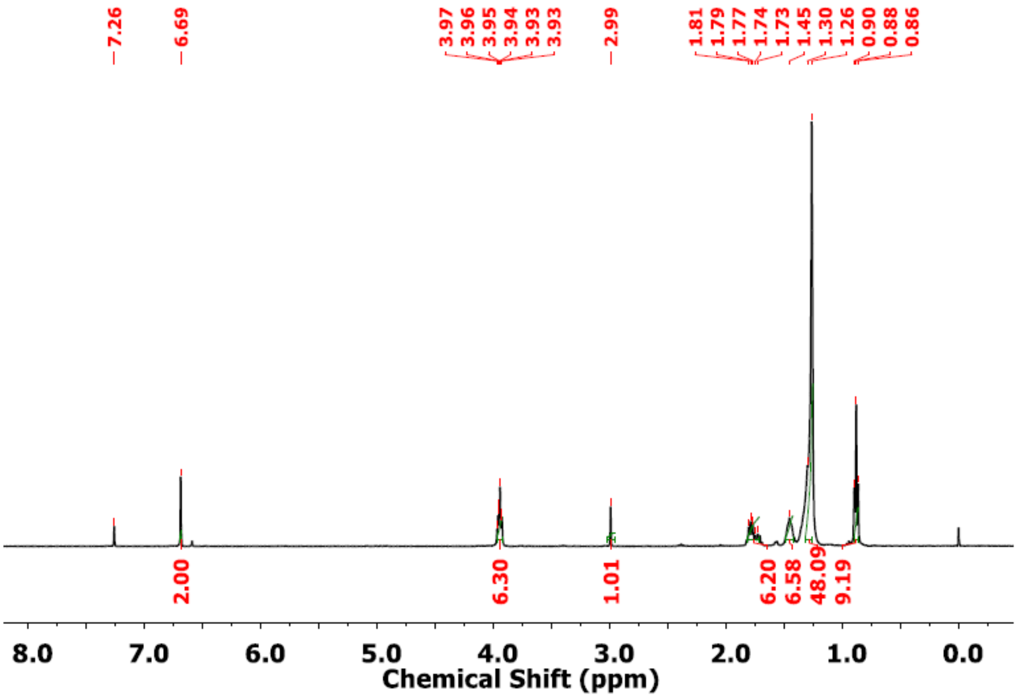

Figure 14 ^{1}H NMR of 1,2,3-tris(dodecyloxy)-5-ethynylbenzene (**7**).

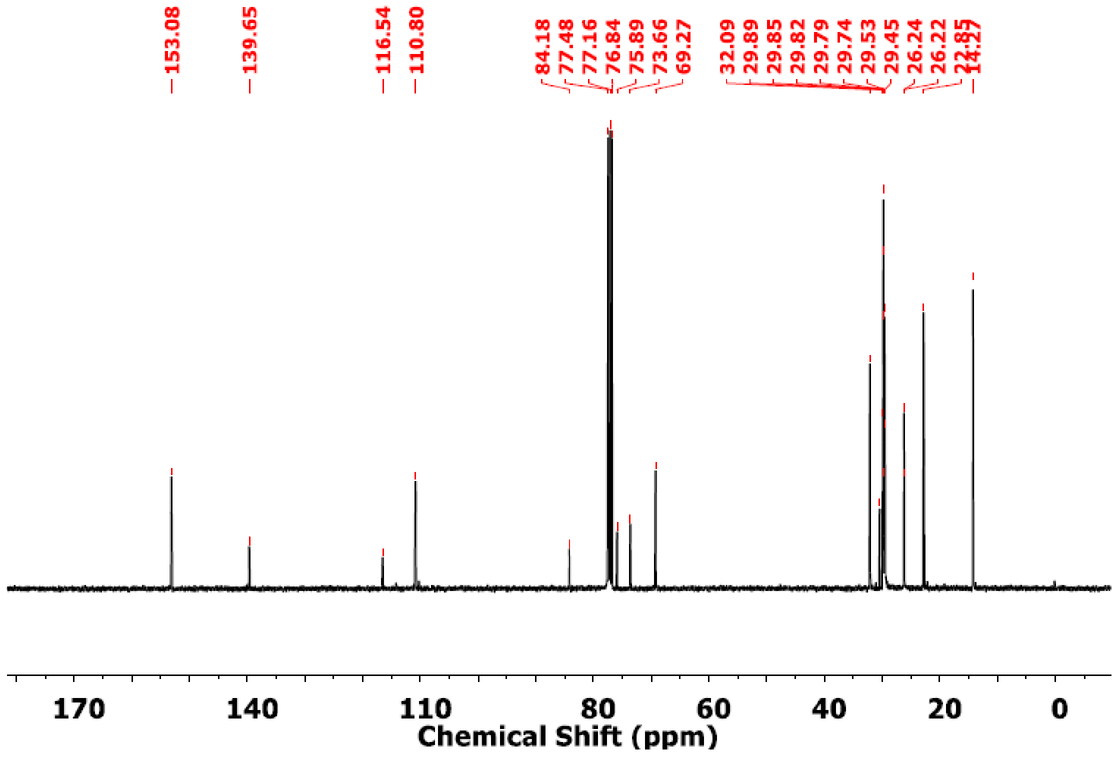

Figure 15 ^{13}C NMR of 1,2,3-tris(dodecyloxy)-5-ethynylbenzene (**7**).

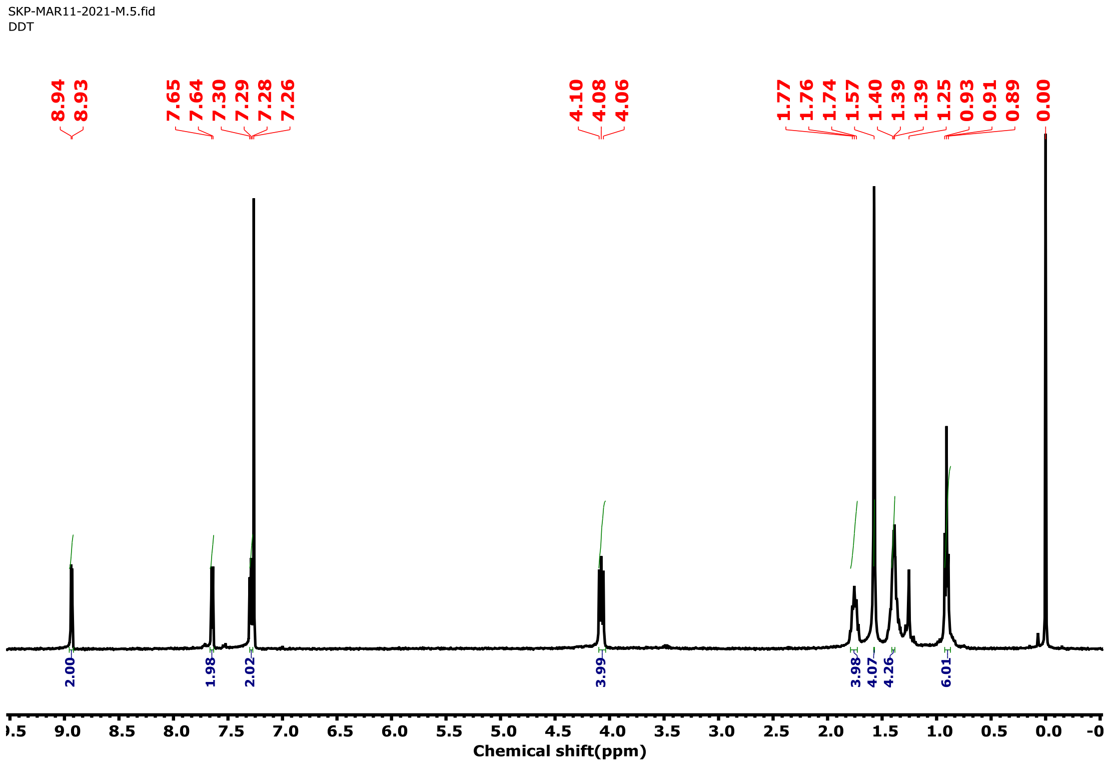

Figure 16 ^{1}H NMR of 2,5-dipentyl-3,6-di(thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione (**3**)

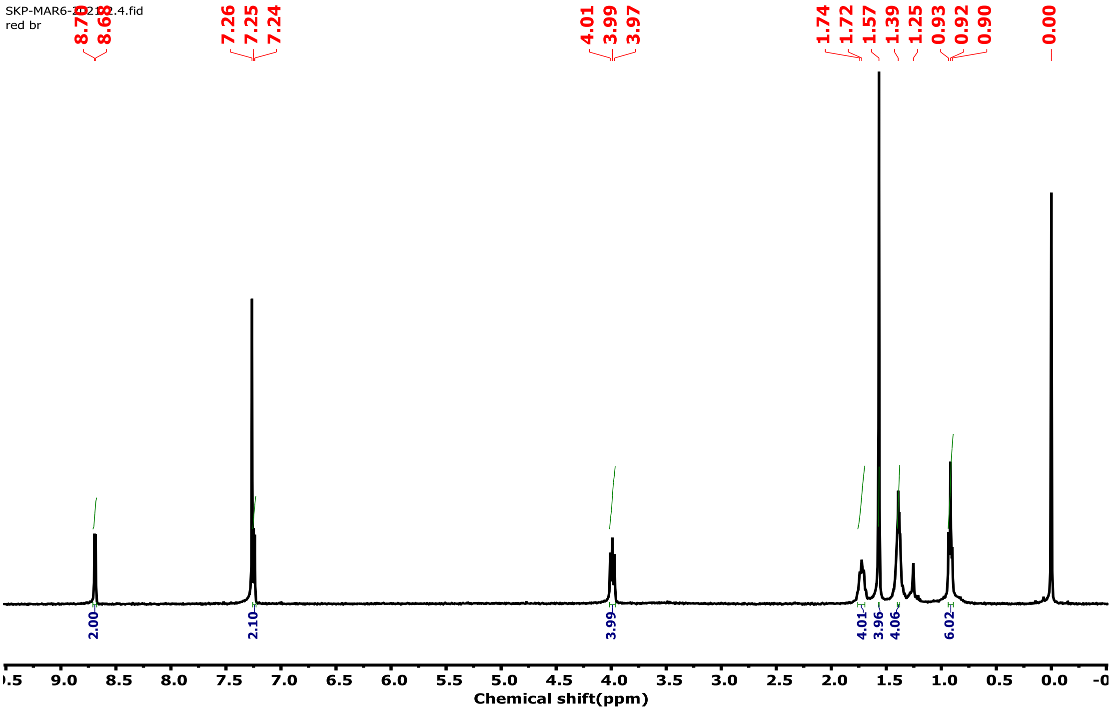

Figure 17 ^{1}H NMR of 3,6-Bis(5-bromothiophen-2-yl)-2,5-di(pentan-1-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4- dione.(**4**)

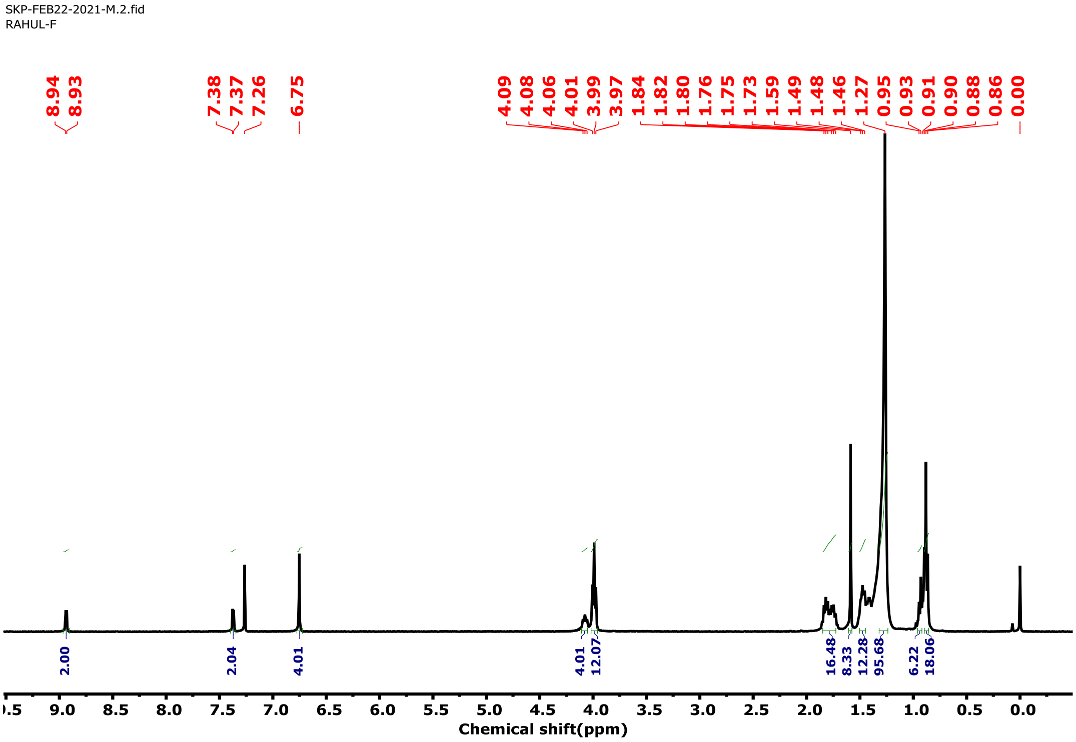

Figure 18 ^{1}H NMR of 2,5-dipentyl-3,6-bis(5-((3,4,5-tris(dodecyloxy)phenyl)ethynyl)thiophen-2-yl)-2,5-dihydropyrrolo[3,4-c]pyrrole-1,4-dione.(**8**)

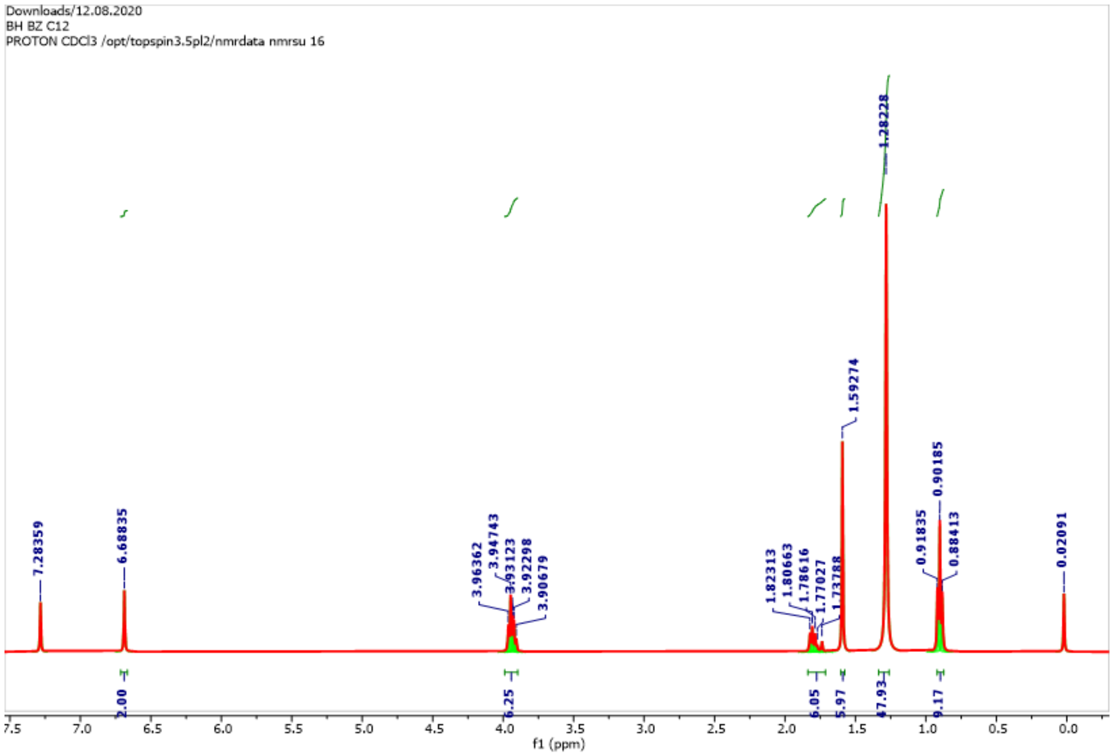

Figure 19 ^{1}H NMR of 1-Bromo-3,4,5-tridodecyloxybenzene(**E**)

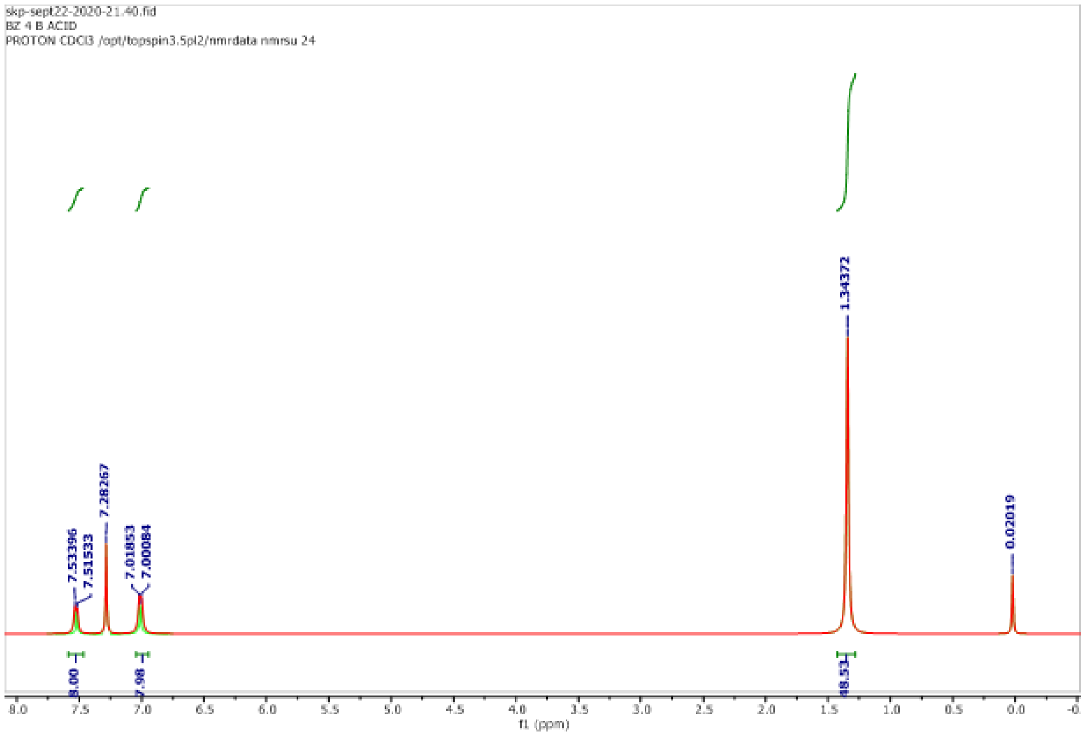

Figure 20 ^{1}H NMR of 1,1,2,2-tetrakis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethene.(**C**)

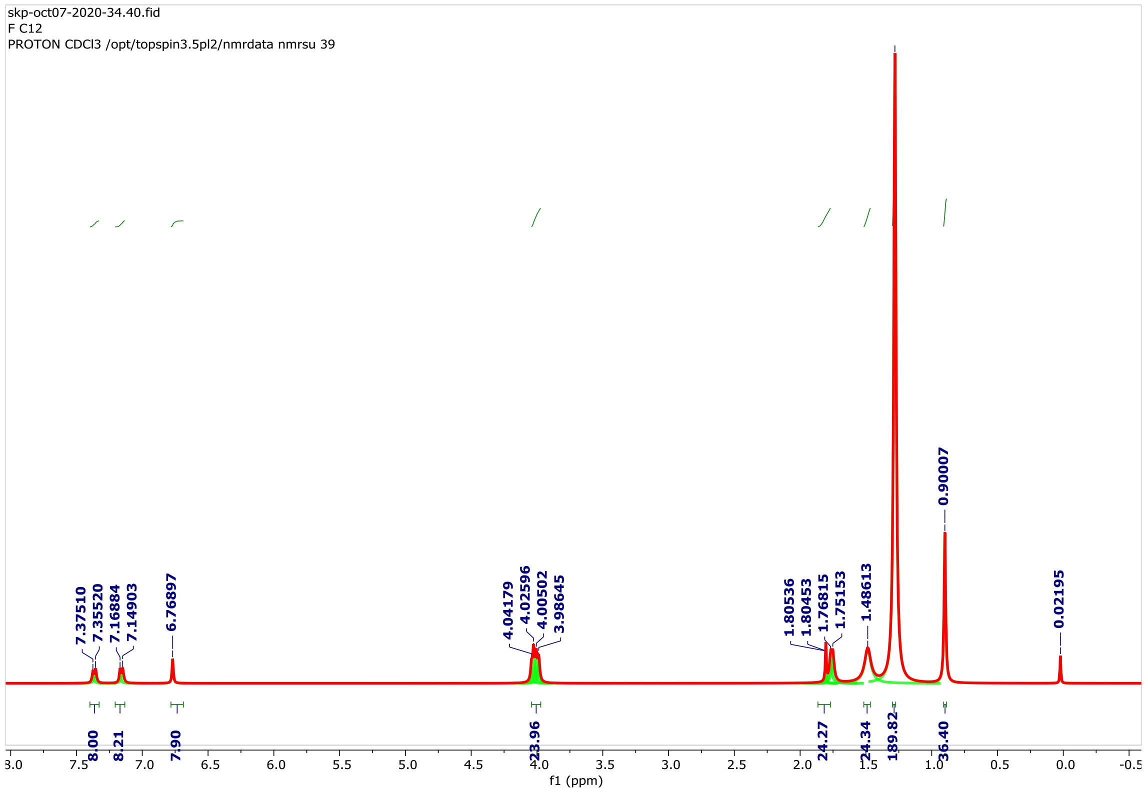

Figure 21 ^{1}H NMR of 1,1,2,2-tetrakis(3',4',5'-tris(dodecyloxy)-[1,1'-biphenyl]-4-yl)ethene (**F**)

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