



Synthesis and Characterization of New 1,3,5-Triazine Derivatives Based on Benzene Ring

Muhammed Abdalhasan Shallal^a, Hyffaa Y. Hussien^b

^aMinistry of Education, Al Nasiriya 64001, DhiQar, Iraq

^bUniversity of Mosul, College of Science, Chemistry Department, Mosul, Iraq



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Abstract

Liquid crystal materials have a number of ordinary uniqueness such as mechanical or electro-optical properties. New triazines derivatives compound was obtained starting from 1,3,5-triazine and 1,3,5-trichlorobenzene. The synthesized compound consists of three-armed based on benzene core built up via cross coupling reaction. The substitution was achieved efficiently at appropriate temperature under the argon atmosphere by cross coupling. However, the two armed of 2,4-bis(dodecyloxy)ethynyltriazine on the periphery are considered for liquid crystal application. The target compound did not exhibit a transition phase in its pure state but, after ionic interaction with 4-DBA which already possess a phase transition, it showed a phase transition and liquid crystal properties. We study the liquid crystal properties of obtained organic salts after ionic interaction through hydrogen bonding via methods of OPM "optical polarizing microscope" and DSC "differential calorimetric scanning". After purification with column chromatography then confirmed their structures by analysis of spectroscopy (MS, NMR, and FT-IR).

Keywords: Tri-armed structure, hydrogen bonding, ionic Interaction, liquid crystal.

Introduction

Liquid crystalline state is matter distinct phase that observed between solid (crystalline phase) and liquid (isotropic); this state has many types depending on the amount of order in the material under investigation [1]. Also, it can be briefly defined as condensed fluid with spontaneous anisotropy [2]. The materials of this state have specific electro-optical properties with low viscosity, low crystalline shape, good solubility, and low melting point [3, 4]. Development of liquid crystals methods is connected with investigation and synthesis of nonconventional liquid crystals based on heterocyclic molecular [5, 6] for example, due to the flexible spacers, tri-armed molecular structures exhibit nematic columnar phase rather than columnar phase. Also, Star shape liquid crystal has small-core and rigid mesogenic units that are preferred for the electro-optical application [7].

In the same manner, Multi-arm molecular liquid crystals attract attention to mesomorphic behavior due to their terminal chain-length of the mesogenic unit and their sensitivity with external electric and

magnetic fields application at low voltages for their uses as sensors and other interesting applications [8, 9]. The fluid nature of liquid crystals is easy in maintaining optical and characteristic properties in thin film at a certain temperature. Also, this type has various characters that differ from trimers, dimers, linear and oligomers compounds such as lower melting temperature, lower viscosity, and good solubility [9, 10]. Molecular weight of branched-arm liquid crystal is higher than the convention allows molecular mass compound which generally consist a few mesogenic units on the core as the sidearm [10-13].

Triazine core, substituted 1,3,5-triazines and benzoic acid mesogenic arms have shown new liquid crystals material [14, 15]. A variety of attached nucleophilic substituents incorporated with cyan uric chloride show discotic and calamitic morphological behaviors depending on their structures [16, 17].

In the field of ionic liquids, the materials that unit the ionic liquids properties and liquid-crystals are considered as ionic liquid crystal which have gain a

*Corresponding author e-mail: moh08790@gmail.com; (Muhammed A. Shallal).

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growing interest in the last decades [18]. There are many applications of ionic liquid crystal such as solvents and batteries using for extraction process, as solar cells to sensitive-dye [19] and fuel cells electrolyte [20].

Supramolecular liquid crystals [21] are molecular complexes that resulted from interaction between independent species via hydrogen bonding. Also, they are able to exist in mesophase due to their binding method electron-rich hydrogen atoms, and the system can be considered as self-complementary [22].

According to above study, we aim to synthesize tri armed triazine derivatives based on six-membered-ring of benzene via cross coupling of Negishi [23] as selective C-C bond formation and study their properties as liquid crystalline phase.

Experimental

Chemistry

All chemicals were purchased from Merck, Sigma Aldrich and used without purification. FT-IR as duced on KBr and was recorded Shiimadzu Prestiige-21, HRMS (High-resolution mass spectrometry), recorded NMR were at Joel TM 500MHz spectrometer as solutions DMSO-d₆ with chemical shift relative to δ . The sonication was done in an ultrasonic using dry THF. Liquid crystalline evaluation of the organic salts was performed using DSC and POM. Reactions were followed via TLC per coated sheets with exposure to UV lamp 254 nanometer for seconds. All compounds chemical names are given as rules of IUPAC. The amount of isolated material via chromatography is a reported yield. Solvents were dried/purified according to conventional procedures.

2-Chlooro-4,6-bis(dodecyloxy)-1,3,5-triazine (1)

A mixture of trichlorotriazine (0.95 g, 5.1 mmol), and K₂CO₃ (1.4g, 10.3mmol) in 10 mL dodecan-1-ol (1.9 g, 10.3mmol) was monitored with TLC on stirring at 50 °C for 5 h. The reaction contents were evaporated, dried and chromatographed.

Eluent: hexane/ethyl acetate: 5%, yield: 1.75g, yield:70%. HNMR (500 MHz, CDCl₃) 3.70 (t, *J* = 6.7 Hz, 12, 4H, OCH₂), 1.8-1.5 (m, 4H, CH₂), 1.4-1.1 (m, 36H, CH₂), 0.94 (t, *J* = 6.9 Hz, 6H, CH₃). ¹³CNMR (126 MHz, CDCl₃) 173, 172, 68.5, 32, 29.7, 29.6, 29.4, 29.3, 28.7, 25.9, 22.7, 14.1. MS: *m/z* M⁺ and [M+K]⁺ calcd for C₂₇H₅₀ClN₃O₂: 483.3; found: 483.3, 523.3 respectively.

2,4-bis(dodecyloxy)-6-ethylenyl-1,3,5-triazine (2)

First step: Me₃SiC₂H₂ (0.17 g, 1.75 mmol) in 3 mL tetrahydrofuran was stirred at 0°C for 1h then n-BuLi (1.10 mL, 1.76 mmol) in hexane was added drop-wise under argon as inert gas sphere. Addition of compound 1 (0.86 g, 1.76 mmol) in 8 mL tetrahydrofuran was done with continues stirring at 0 °C for 2h under argon gas then, warm up to the room temperature to get 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (1) which was directly used without purification and isolation.

Second Step: the corresponding compound (0.90 g, 1.65 mmol), and K₂CO₃ (0.68 g, 4.95 mmol) in MeOH/THF (v:v, 50:50) was stirred 24 h. at room temperature. This residue was cooled, evaporated and chromatographed with hexane/ethyl acetate (60:40) as elution, the material obtained was purified to obtain yellow liquid materials of compound 2 with a yield (0.7 g, 42%). ¹HNMR (500 MHz, CDCl₃) 3.9 (s, 1H), 3.5 (t, *J* = 6.6 Hz, 4H, OCH₂), 1.5-1.39 (m, 4H, CH₂), 1.4-1.0 (m, 36H, CH₂), 0.78 (t, *J* = 6.8 Hz, 6H, CH₃) ppm. ¹³CNMR (126 MHz, CDCl₃) 174, 173, 74, 69, 63, 32, 30.2 (2C), 30.0 (2C), 29.6, 29.2, 27.3, 26, 23, 14.6) ppm. MS = *m/z* [M+H]⁺ calcd for C₂₉H₅₁N₃O₂: 473.40; found: 474.4.

1,3-Dichloro-5-phenoxybenzene(5)

Trichlorobenzene 3 (2.0 g, 11.1 mmol), phenol (4) (1.04 g, 11.1 mmol) and K₂CO₃ (3.37 g, 24 mmol) in 10 mL of dioxane in the presence of palladium catalyst was stirred for 6h at 90°C under argon. Temp. raised 100 °C in 4 h. Then mixture was cooled and organic layer extracted with ethyl acetate, dried, evaporated then chromatographed with hexane/ethyl acetate as elution, the material obtained was purified to afford colorless crystals (2.0 g, 82%). ¹H NMR: (CDCl₃) 7.27 (s, 3H, Ar-H), 7.22 (d, *J* = 8.5 Hz, 2H, Ar-H), 6.8 (d, *J* = 8.8 Hz, 3H, Ar-H). HRMS = M⁺ calcd for C₁₂H₈Cl₂O:238. (2M⁺) found = 477.982 (477.982 - 2 = 238.9) and (3M⁺) found = 715.9 (715.9 ÷ 3 = 238.3).

6,6'-((5-phenoxy-1,3-phenylene)biis(etheyne-2,1-diyl))bis(2,4-bis(dodecyloxy)-1,3,5-triazine) (6)

Compound 5 (0.08 g, 0.23 mmol), compound 2 (0.22 g, 0.47 mmol), Pd(PPh₃)₄ (0.026 g, 0.024 mmol), CuI (0.09 g, 0.05 mmol) and K₂CO (0.06 g, 0.43mmol) were dissolve in 10mL of dioxane (Scheme 1). The reaction was stirred at 80°C for 16h. The mixture was

cooled organic layer extracted with ethyl acetate, dried, evaporated then chromatographed with hexane/ethyl acetate as elution, the material obtained was purified to give a solid material as product title (0.2 g, 80%). FT-IR: 2915, 2847, 1710, 1572, 1552, 1470, 1415, 1320, 1114 cm^{-1} . ^1H NMR: 7.4 (s, 2H, H_{arom}), 7.3 (s, 1H, H_{arom}), 7.2 (m, 5H, H_{arom}), 4.1 (t, $J = 6.7$ Hz, 8H, OCH_2), 1.6 (m, 16H, CH_2), 1.3- 1.1 (m, $J = 7.0$ Hz, 64H, CH_2), 0.6 (t, $J = 6.6$ Hz, 12H, CH_3). ^{13}C NMR: 173, 171, 151, 133.8, 133.5, 130, 123.8, 123, 121, 102.6, 98, 69, 32, 30.16, 30, 15, 30.1, 29.8, 29.7, 29.1, 26.3, 23.2, 14.6. HRMS = M^+ calcd for $\text{C}_{70}\text{H}_{108}\text{N}_6\text{O}_5 = 1112.8$, (M) $^+$ found = 1112.8 and ($\text{M}+\text{K}$) $^+$ found = 1151.79 (1151.79-39= 1112.79).

Preparation of 4-(dodecyloxy) benzoic acid (4-DBA) (7)

4-OH-benzoic acid (2.1 mmol), 1-bromododecane (1.45 mL, 11.5 mmol, 2.9 g), and KOH (0.3 g, 11.5 mmol, 2.9 g) in 10 mL EtOH was refluxed for 72 h (TLC). The mixture was hydrolyzed with potassium hydroxide (25 mL) under refluxing overnight then, with HCl (6 M), the mixture was acidified and cooled to room temperature. Recrystallized of the precipitate from EtOH to yield a colorless pure product, 0.5 g, 90% yield. ^1H NMR (500 MHz, CDCl_3) 8.03(d, $J=8.8$ Hz, 2H, H_{arom}), 6.9 (d, $J=6.8$ Hz, 2H, H_{arom}), 4.03 (t, $J=6.4$ Hz, 2H, OCH_2), 1.9-1.6 (m, 2H, CH_2), 1.5-1.1 (m, 18H, CH_2), 0.87 (t, $J=7.0$ Hz, 3H, Me).

Preparation of Compound organic salt 8

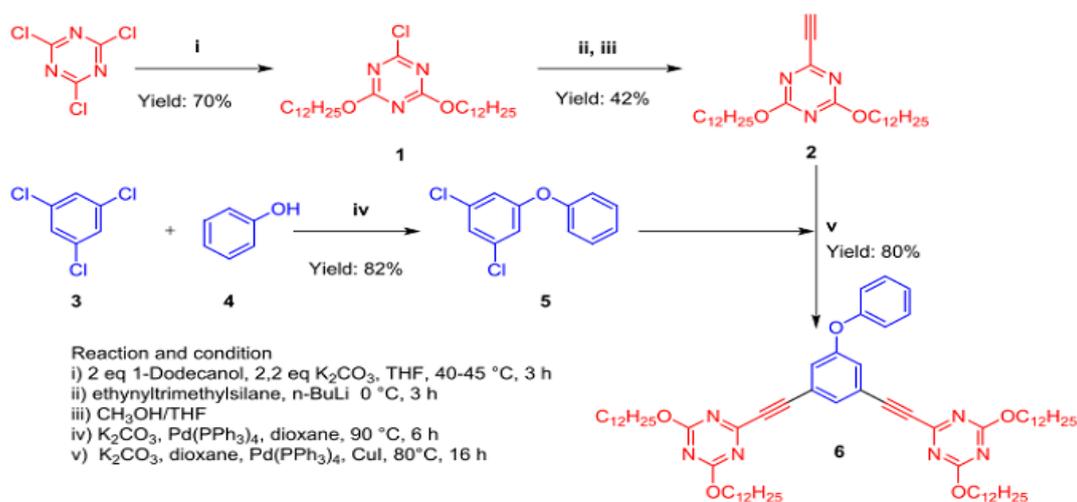
Compounds **6** and **7** with one to two ratio (Scheme 2). In dry THF, the sonication was done until a transparent solution was obtained. FT- IR: 2914, 2848, 2562, 1671, 1604, 1577, 1556, 1512, 1418, 1376 cm^{-1} . ^1H NMR: 7.8 (d, $J = 8.9$ Hz, 2H, H_{arom}), 7.4 (s, 2H, H_{arom}), 7.0 (m, 6H, H_{arom}), 6.7 (d, $J = 8.9$ Hz, 2H, Ar-H), 4.15 (t, $J = 6.7$ Hz, 8H, OCH_2), 3.8 (t, $J = 6.6$ Hz, 2H, OCH_2), 1.6 (m, 14H, CH_2), 1.2 - 1.1 (m, 86H, CH_2), 0.7 (m, 15H, Me). ^{13}C NMR: 173, 172, 171, 163, 134, 133.6, 133.2, 132, 126, 123, 122, 121, 114, 97.8, 68.8, 68.5, 32.2, 29.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 28.6, 28.3, 22, 14.4. HRMS = M^+ calcd for $\text{C}_{89}\text{H}_{138}\text{N}_6\text{O}_8$: 1419. ($\text{M} + 3$) found = 473.35 (473.35 x 3 = 1420), and ($\text{M} + 3\text{K}$) $^{+3}$ found = 512.3 (512.3 x 3 - 39 = 1420).

Results and Discussion

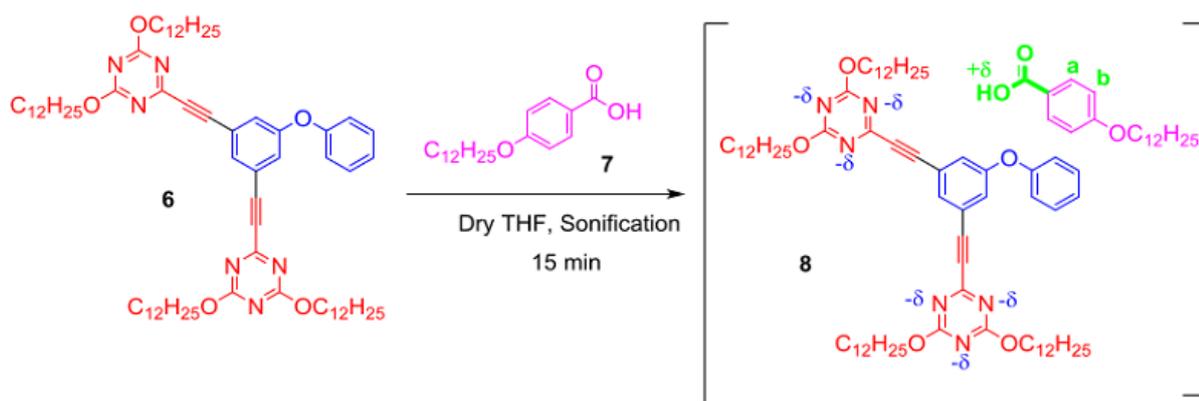
2,4,6-trichloro-1,3,5-triazine reacted in molar ratio

with 1-dodecanol at 40-45°C in tetrahydrofuran for 3h to afford 2-chloro-4,6-bis(dodecyloxy)-1,3,5-triazine (**1**), this compound reacted with ethynyltrimethylsilane to get 2,4-bis(dodecyloxy)-6-ethynyl-1,3,5-triazine (**2**) in good yield (Scheme 1). 1,3,5-Trichlorobenzene reacted with phenol to afford 1,3-dichloro-5-phenoxybenzene (**5**) (Scheme 1). Compound **1** and phenoxybenzene derivative **5** reacted together in dioxan to get 6,6'-((5-phenoxy-1,3-phenylene)bis(ethyne-2,1-diyl))bis(2,4-bis(dodecyloxy)-1,3,5-triazine) (**6**) 1:2 ratio to increase possibility of the liquid crystal which showed at low temperature. Structures of new compound were confirmed with NMR and HRMS techniques (cf. Experimental).

Ionic interaction is confirmed via reaction of compound **6** with 4-(dodecyloxy) benzoic acid (4-DBA, **7**) in Sonification for 15 min in dry THF to afford transparent solution of compound **8** (Scheme 2). Structures of new compounds were elucidated upon NMR, HRMS, and FTIR spectroscopic data. FTIR spectrum of 4-DBA, compound **6** and **8** is depicted in figure 1 that shows ionic interaction between them and revealed carboxylic acid group at 1572 cm^{-1} in compound **6** then shifted to 1680 then 1871 in 4-DBA and **8** respectively



Scheme 1: Synthesis Procedure of Tri-armed Structure



Scheme 2: Synthesis route of organic salt

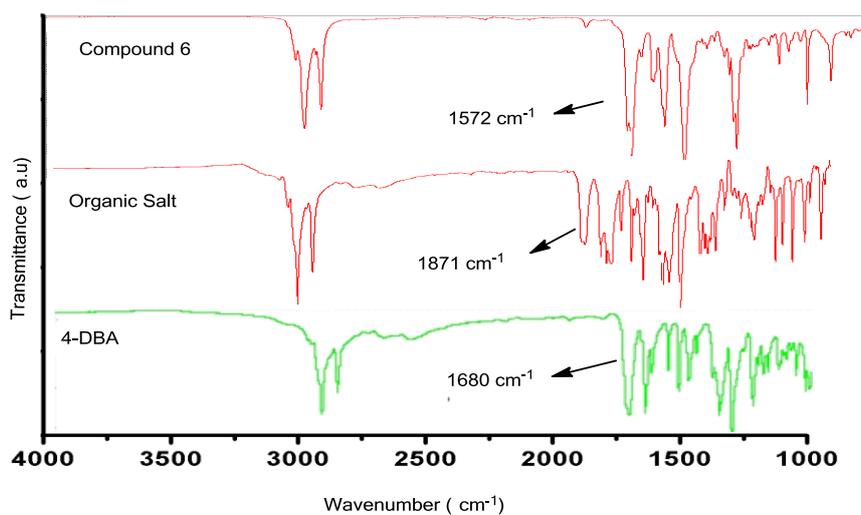


Figure 1: Shifting of FT-IR spectrum

In addition, HRMS spectrum of compound 8 revealed peaks at $m/z = 473$ and 512 for $[\text{C}_{89}\text{H}_{138}\text{N}_6\text{O}_8]^{+3}$ and $[\text{C}_{89}\text{H}_{138}\text{N}_6\text{O}_8]+3\text{K}]^{+3}$ respectively (Figure 2).

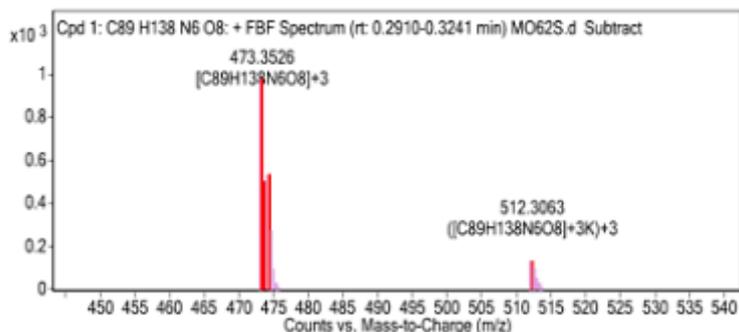


Figure 2: HRMS spectrum of the organic salt (8)

The aromatic protons signals of 4-DBA unit after ionic interaction shifted from (8.02, 6.9) ppm in the pure state to the higher field at (7.7, 6.8) ppm in organic salt state. As a result of ionic interaction between carboxylic and triazine of the mesogenic unit which cause increment in aromatic ring electron density to

achieve, shifting of aromatic protons in organic salt. Besides, the oxymethylene (OCH_2) peak which belongs to the 4-DBA unit at pure state observed at 4.02 ppm, and then further shifted to 3.73 ppm in organic salt after the ionic interaction. (Table 1).

Table 1: chemical shifts of revealed proton

Compound	$T/^\circ\text{C}$ [ΔH kJ/mol]
4-DBA ^b	H \rightarrow : Cr 100 SmC 133 N 139 [2.1] Iso
OS (8)	H \rightarrow : Cr 29 [-32] Col Cr 4.7 [-36.4] Col 36.8 [-32.5] Iso: \leftarrow C

^bPerkin-Elmer DSC-6; enthalpy values a rate of $10^\circ\text{C min}^{-1}$; SmC stands for tilted smectic phase, Cr stands for crystalline, Col is for columnar mesophase, and Iso stands for isotropic liquid phase.

For confirmation, ^{13}C NMR revealed shifting of carbonyl group to 171.2 ppm in 8 and at 171.8 as a result of increment of electron density and decreasing in carbon electron density of ionic interaction form to slightly shift aromatic carbon next to alkoxy group from 163.69 to 163.9 ppm to confirm organic salt 8. 4-DBA was used in this reaction for increment of the possibility of liquid crystalline [24]. On the heating cycle of compound 7, three-peaks were observed related to Cr, Sm, C-N Iso transitions. On the cooling cycle from the isotropic phases, the same behaviour of reverse transitions was observed. Besides, on the

cooling cycle from isotope a peak detected at 65.86°C which corresponding to the Cr-Cr transition [25]. A typical texture of SmC mesophase observed for 4DBA are shown in (Figure 3).

The transition phase of salt 8 showed two peaks on heating curves between (36.79 - 4.77) $^\circ\text{C}$ and one peak was observed at 29.58°C on cooling from the isotope phase. The transition phase determined by differential scanning calorimetry (DSC), two an endothermic peak and one peak on the cooling cycle, which confirm the liquid crystalline of 8 (Table 2).

Table 2: Phase transition of the organic salts 8 and 4-DBA.

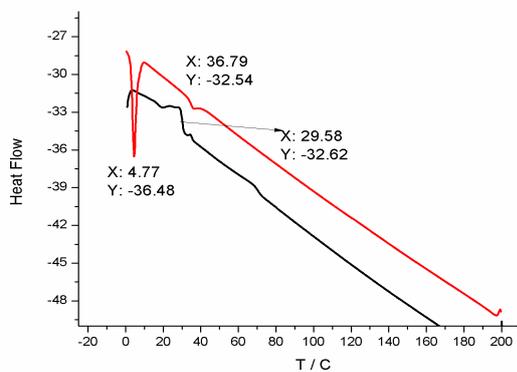
Compound	$\text{H}^{\text{a}}_{\text{arom.}}$ (ppm)	$\text{H}^{\text{b}}_{\text{arom.}}$ (ppm)	OCH_2 - (ppm)
6	-	-	4.02
4-DBA	8.02	6.92	4.15-3.97
8	7.70	6.8	3.73

Molecular crystalline liquid depends upon its side chains as its chain increases, temperature of transition phase decreases. Therefore, the molecular structure

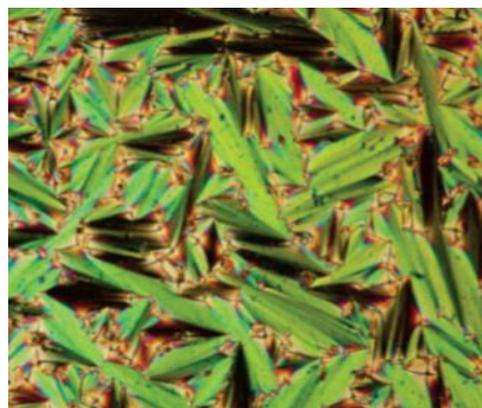
with a long alkoxy side chain that obtained via ionic interaction showed liquid crystalline properties at low temperature [25]. The ionic liquid crystals showed low transition temperatures which are more ordered than

the smecticA phase at a lower temperature. However, ionic interactions have a tendency to steady lamellar mesophases [26]. The organic salt is a result of a non-covalent intermolecular interaction of the star-shaped compound 8 and n- dodecyloxy terminal chain of 4-DBA. Ionic interaction has shown good properties on mesogenic properties such as clearing temperatures

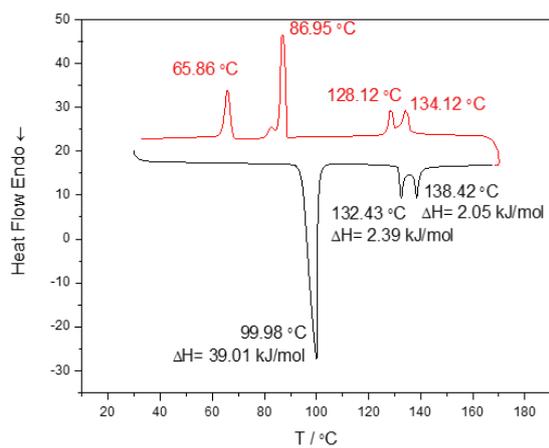
and melting as well as inducing the columnar phase at lower temperatures. The texture which observed refers to the Col phase which appeared at about $T = 29^\circ\text{C}$ and completely disappears and the crystalline phase appeared at 38°C (Figure 3).



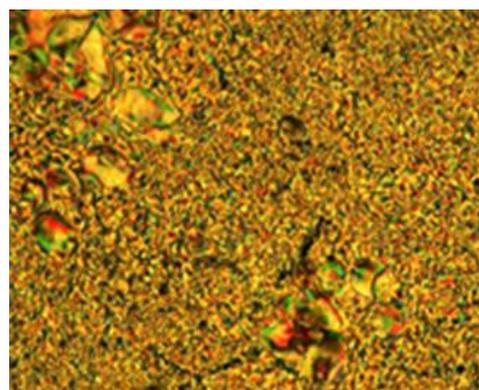
(a)



(b)



(c)



(d)

(a) organic salt 8, (b) Optical textures of organic salt 8 at 45°C , (c) 4-DBA on 1st heating and cooling ($10^\circ\text{C min}^{-1}$), (d) A typical texture of the smectic C mesophase of compound 4-DBA $T = 118.0^\circ\text{C}$

Figure 3: DSC thermograms and optical texture

Conclusion

Based on benzene ring, tri-armed structure was synthesized successfully via cross-coupling reactions. The obtained tri-armed was connected to the one arm of phenoxy group and two arm of triazine unit which carrying dialkoxy groups at the periphery. The product was non-liquid crystal compound. To rise the liquid crystal possibility, 4-DBA was added 1:2 ratio. Ionic interaction via hydrogen bonding explains columnar mesophase formation between 8 and 4-DBA carboxylic acid group. Star shaped compound 6 act as proton acceptor

and carboxylic acid group of 4-DBA with its side chain act as proton donor. At lower temperature, Ionic interactions have a deep influence upon mesogenic properties and inducing a columnar phase. However, presence of side chain alkoxy group causes lowering of mesophase transitions to linear alkyl chain which is usually obtained via hydrogen bonding in the liquid crystals applications at low temperature.

Conflicts of interest

There are no conflicts to declare.

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