



New macromolecular structures based on benzene core, synthesis and characterization

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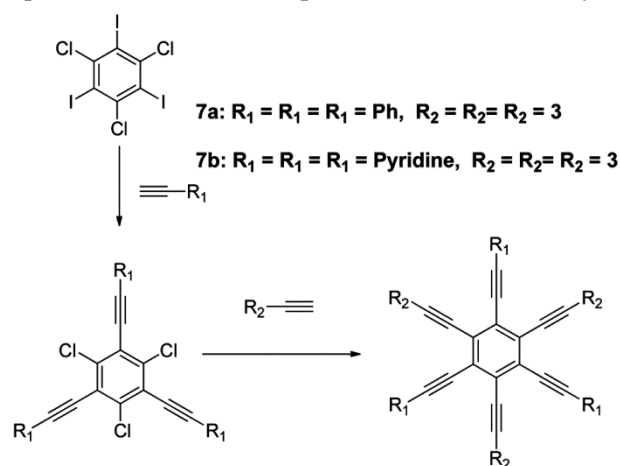
A series of new compounds based on benzene ring as a central core substituted with aromatic compounds such as (benzene and pyridine) and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine, have been obtained by sequential nucleophilic substitution of chlorine atoms in cyanuric chloride. The substitution at the acetylenic periphery on the central benzene ring has been achieved efficiently by Sonogashira coupling. Equimolar mixtures of the six-armed compounds based on the benzene core with the complementary 4-dodecyloxybenzoic acid, which already possessed liquid crystal property, has resulted in an organic salt. The obtained organic salts have been investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). The synthesized compounds have been confirmed by spectroscopic methods (¹H and ¹³C NMR and mass spectrometry).

Keywords: Triazine, liquid crystals, hydrogen bonding, synthesis, characterization

Liquid crystals are unique in their properties and uses which has an important role in the area of technological applications such as electrical, optical, displays, temperature maps, and switching materials^{1,2}. The chemistry of triazine has gained increased attention in the last few decades, due mostly to their applications in organic synthesis and liquid crystal properties which has application in many areas³. Following that, recent years has been also focused on the hexa-ethynylbenzene derivatives due to their potential as liquid crystals⁴, nonlinear optical material⁵, core structures for dendritic⁶, as well as light-harvesting materials⁷, and building blocks for two-dimensional carbon networks⁸. Substituted hexa-ethynylbenzenes, in which the ethynyl ends possess different functional groups are attractive because it would be possible to change the above properties by modifying the substitution pattern of the terminal groups⁹. The more frequently utilized nucleophilic substitution reactions have been mostly limited to amines and alcohols so far, providing selective substitution at the price of decreased cycloaddition ability due to the electron-donating nature of the new substituent¹⁰.

Our research program on the construction of extended π -electronic systems, we planned to synthesis hexaethynylbenzene derivatives starting

from 1,3,5-trichlorobenzene benzene as a central core substituted with three aromatic ring and three armed of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine (Scheme I). These molecules are formed by the covalent linking of three arms symmetrically to a central core. These arms may be linked to the central core through flexible or semi flexible or rigid linkers. When the central core connecting to the linkers and three rigid arms, shape persistent star shaped mesogens are obtained¹¹. These molecules lack the shape anisotropy of discotics required to exhibit mesophases, but their ability to



Scheme I — Synthetic route of six arms compounds

form mesophases is supported by the nanophase segregation of chemically or physically different molecular subunits and their tendency to fill the space efficiently in bulk¹². The advantage of this molecular design with concering to discotic is the synthetic flexibility provided to incorporate various functional units into the molecular structure.

Result and Discussion

The intermediate compound **2** was confirmed by the presence of $(M+H)^+$ peaks at 424.27. Also, the corresponding singles of oxymethylene peak observed at δ 4.5 as triplet, wherease, hydrogen double bond peak appeared at δ 5.1. In the ¹³C NMR, the triazine and OCH₂ peaks are observed at δ (172, 171, 69) respectively, while the double bond peaks appear at δ (131.5, 124.3).

However, the molecular weight of compound **3** was confirmed by the presence of $(M+H)^+$ and $(M+Na)^+$ peaks at 486.33 and 508.32 respectively.

The aromatic proton peaks of benzene ring (**6a**) observed at δ (7.6, 7.4) as doublet and multiplet repectively. However, the triple bond peaks of carbone was observed at δ (81.6, 74). Besides, five peaks of aromatic carbon corresponding to benzene ring appears between δ (142-121). The molecular weigh of compound detected by $(M+H)^+$, peaks at 483.02.

The molecular wieght of compound (**6b**) confiremd by $(2M^+)$ peak at 968.0178. The corresponding proton singnals of aromatic ring oberved at δ (7.4, 7.25) as a doublet and multiplet respectively. In the ¹³C NMR the triple bond peaks was observed at δ (100, 97.9), while the aromatic carbon showed seven peaks between δ (145-128).

Structure of compound (**7a**) proved by the presence of $(M+3H)^{+3}$ peaks at 538.34. Besides, the aromatic proton signals appeares at δ 7.4 as a doublet and δ 7.2 as a multiplet, while the (OCH₂) peak appears at 4.2 as a triplet. In addition, the proton on double bonds carbon showed singlet peak at δ 4.8 as a singlet. The triazine carbon peaks were observed at δ (172.2, 170.5), whereas signals corresponding to triple bond carbon showed four peaks between δ (88.5-74.4), while five peaks was observed between δ (133-122) belonging to aromatic ring. Inaddition, the double bond carbon observed at δ (131, 128), and the OCH₂ peak appears at δ 66.8.

Structure of compound (**7b**) proved by the presence of $(M+3Na)^{+3}$ peaks at 561.98. The singnals corresponding to aromatic proton detected at δ 7.5 as a doublet and δ 7.15 as a doublet, while the

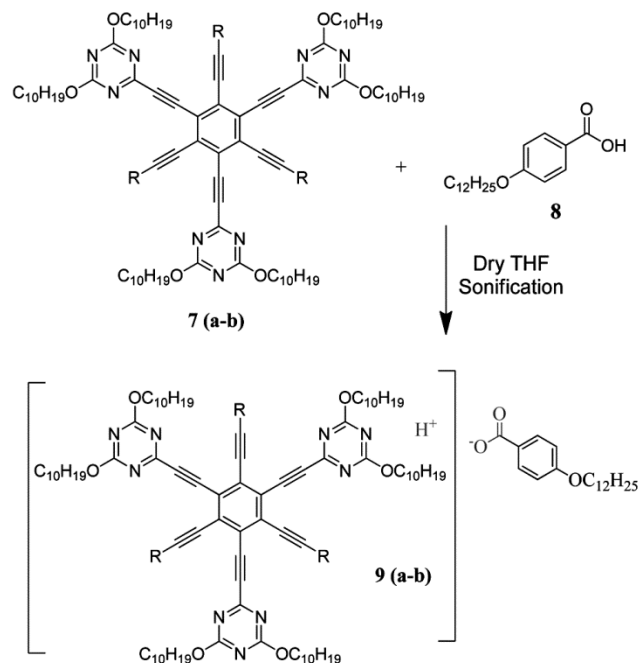
oxymethylene signal appears at δ 4.2 as a triplet. In addition, the proton on double bonds carbon showed singlet peak at δ 4.85. The triazine carbon peaks were observed at δ (171.7, 171.2). Three triple bond peaks appear at δ (99.5, 99.3, 82), while the aromatic carbon showed seven peaks between δ (142.5 -121.9). In addition, the double bond carbon observed at δ (131, 124), and the (OCH₂) peak observed at δ 67.

Synthesis of Organic Salt

4-DBA mesogenic unit (**8**) reacted with **7(a-b)** in 10 mL of dry THF with one to one ratio (Scheme II). The resulting solution was sonicated for 15 min until observing a transparent solution. Then, the solvent was removed in vacuum.

The formation of ionic interaction between the six-armed π -conjugated system and the mesogenic carboxyl group was mainly studied by FT-IR. The carboxylic peak corresponding to 4-DBA at 1670 cm⁻¹ shifted to 1566 cm⁻¹ in both organic salt (**9a**, **9b**). Whereas, the stretching vibration of the C=C bond of both organic salt appears at 1675 cm⁻¹ and 1635 cm⁻¹ (Figure 1). Besides, peaks at 2900 and 2800 cm⁻¹ belonging to hydrogen stretching¹³.

Also, NMR spectroscopy confirmed the formation of organic salt (**9a**, **9b**). The signals belong to the aromatic protons of alkoxy benzoate unit in both compounds shift to δ (7.8, 6.7) and δ (7.9, 6.75)



Scheme II — Synthetic procedure for organic salts (9a, 9b)

respectively as compared with the signals of pure 4-DBA at δ (8.05, 6.95), due to increase in electron density of aromatic ring. Similarly, the signals of oxymethylene protons of 4-DBA in ion complex shift to higher field δ 3.8 and 3.75 as compared with the signals of pure 4-DBA at δ 4.05 (Figure 2). Additionally, the singlets of aromatic ring protons in organic salt (**9a**, **9b**) didn't show any shifting due to their electronic environment did not change. These change in chemical shift related to the difference in electron density after the interaction.

However, the ^{13}C NMR spectra show that the carbonyl carbon of 4-DBA shifted from δ 171.6 to 165.12, similarly the aromatic carbon next to alkoxy group of 4-DBA shift slightly from δ 163.69 to 163.6. These change in chemical shift due to decrease of electron density after the ionic interaction (Figure 3).

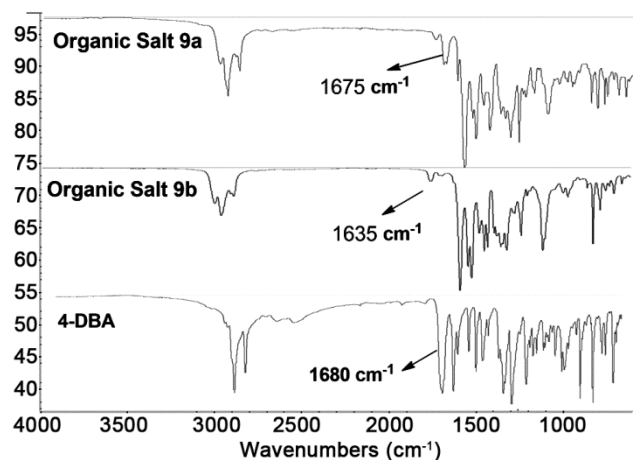


Figure 1 — FT-IR spectra of organic salt (9a, 9b) and benzoic acid (4-DBA)

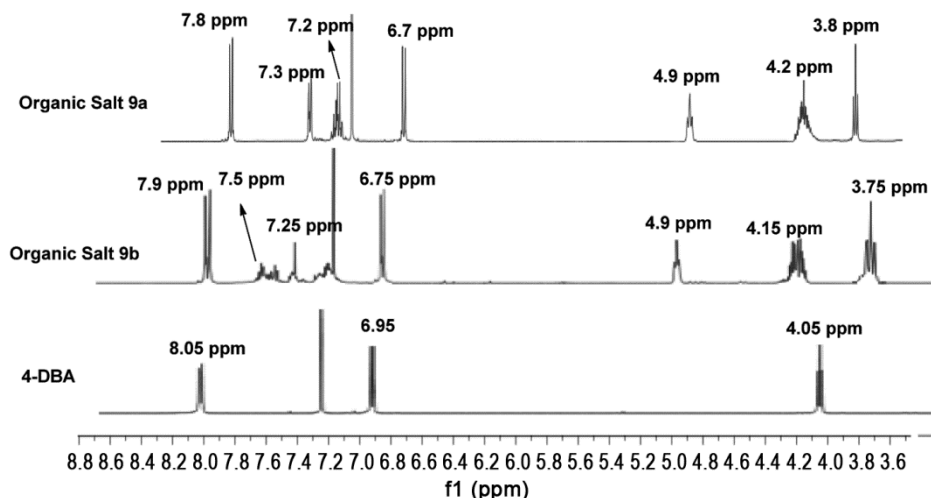


Figure 2 — The comparison of ^1H NMR spectra (in CDCl_3) of organic salts (9a, 9b) and benzoic acid (4-DBA)

Additionally, the peaks which belong to triazine ring didn't show any shifting.

Additionally, the mass spectrometry of organic salt (**9a**) confirmed the molecular structure by the presence of $(\text{M}+3\text{K}) +3$ at 678.70 peaks, which correspond to $\text{C}_{124}\text{H}_{159}\text{N}_9\text{O}_9$, similarly the molecular structure of organic salt (**9b**) confirmed by the presence of $(\text{M}+3\text{K}) +3$ peaks at 680.36 and 680.03, which correspond to $\text{C}_{121}\text{H}_{156}\text{N}_{12}\text{O}_9$, (Figure 4).

Compound 4-DBA, which has a terminal chain, and already shows liquid crystalline, so in order to obtain liquid crystalline material for our synthesized compounds, the equimolar mixture between six-armed π -conjugated system and 4-DBA was obtained through ionic interaction. Concerning to 4-DBA, upon heating showed three peaks corresponding to Cr–SmC–N–Iso transitions. On cooling from isotropic phase, the same behavior of reverse transitions was observed (Table I). In addition

Table I — Mesophases and phase transition temperatures as observed on heating (H \rightarrow) and cooling (\leftarrow C) and corresponding transition enthalpies of organic salts (9a, 9b) and 4-DBA

Compd	T/ $^{\circ}\text{C}$ [ΔH kJ/mol]
4-DBA ^b	H \rightarrow : Cr 99.98 [39.01] SmC 132.43 [2.39] N 138.42 [2.05] Iso
OS (9a)	H \rightarrow : Cr 52 [170.46], Col 81.53 [22.4] Iso Cr 16.30 [142.59] Col 69 [11.2] Iso: \leftarrow C
OS (9b)	H \rightarrow : Cr 25.2 [190.46], Col 78.4 [19.4] Iso Cr 18.2 [182.73] Col 64 [13.2] Iso: \leftarrow C

^aPerkin-Elmer DSC-6; enthalpy values in italics in brackets taken from the 1st heating and cooling scans at a rate of $10^{\circ}\text{C min}^{-1}$; Abbreviations: Cr = crystalline, SmC= tilted smectic phase, N = nematic phase; Col= columnar mesophase, Iso = isotropic liquid phase.

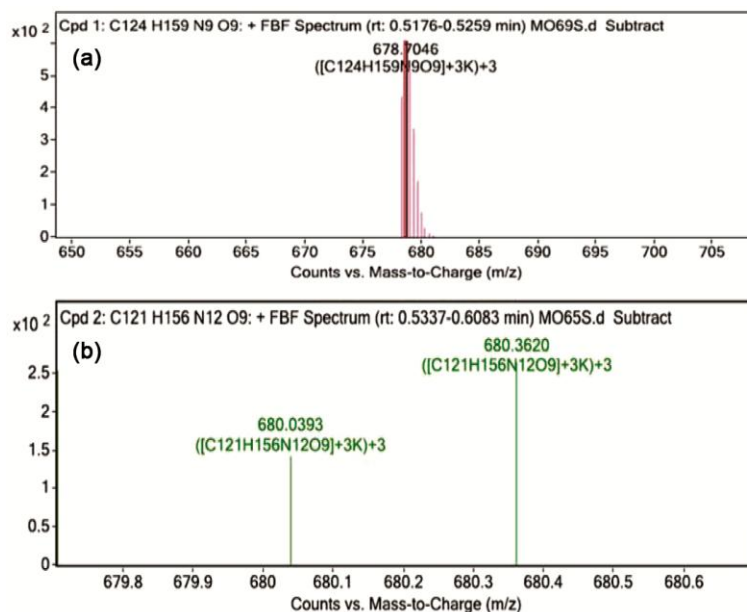


Figure 4 — HRMS result of organic salt (9a, 9b)

to this, a calorimetric peak corresponding to Cr-Cr transition at 65.86°C was detected in cooling DSC thermogram^{14,15}.

The equimolar mixtures of the organic salt (**9a,9b**) based on the benzene core were investigated by using optical polarizing microscope, (PM) and differential scanning calorimeter (DSC). The compounds (**9a, 9b**) show one endotherm corresponds to crystal to the isotropic (Iso) transition in heating DSC thermogram. The organic salts (**9a, 9b**) show no liquid crystal behaviour by an optical polarizing microscope (PM) observation.

The Organic salt (**9a, 9b**) exhibit a phase transition sequence of Cr-Col-Iso which is in agreement with two endotherms in DSC heating curves. Compound (**9a**) on cooling from the isotropic liquid, exhibited one peak in phase transition with the dendritic growing texture was observed between (64-18)°C, whereas compound (**9b**) phase transition with the dendritic growing texture was observed between (71-20)°C (Figure 5).

Experimental Section

Cyanuric chloride, dodecan-1-ol, ethynylbenzene, 1,3,5-trichlorobenzene, 2-iodothiophene, 2-ethynylpyridine, ethynyltrimethylsilane, copper iodide, potassium carbonate, tetrakis(triphenylphosphine) palladium and triethylamine. The solvents were used dry (THF, Dioxane) were obtained from distilling over phosphorous pentoxide (Merck). Homogeneity of the compounds was checked by TLC on silica gel 60 F₂₅₄

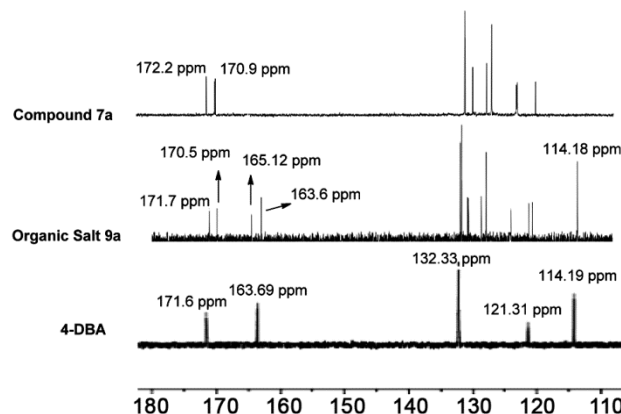
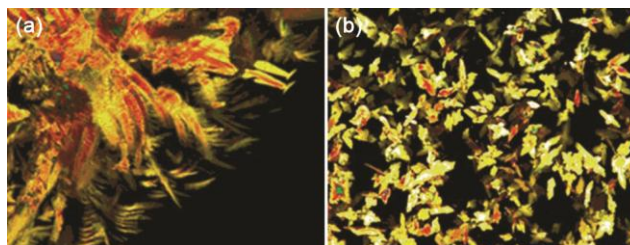
Figure 3 — ¹³C NMR spectra (in CDCl₃) of compound 7a, organic salt (9a) and benzoic acid (4-DBA)

Figure 5 — Optical textures of organic salt [9a (left), 9b (right)] as observed between crossed polarizers in an ordinary glassplates

(Merck). Synthesized compounds are characterized by ¹H NMR and ¹³C NMR spectra using CDCl₃ as a solvent with TMS as an internal standard. IR spectra were recorded in KBr on a Shimadzu FTIR 8400S

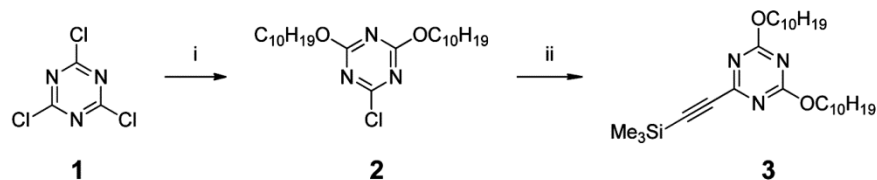
spectrophotometer. Mass spectra were recorded on a GCMS-QP 1000 mass spectrometer.

2-Chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine, 2

A mixture of 2,4,6-trichloro-1,3,5-triazine (**1**) (0.295 g, 1.59 mmol), 3,7-dimethyloct-6-en-1-ol (0.5 g, 3.199 mmol) and K_2CO_3 (0.45 g, 3.2 mmol) were dissolved in 10 mL of THF under argon atmosphere and stirred at 50°C overnight (Scheme III). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation was dried with anhyd. Na_2SO_4 . Under vacuum, the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to yield (0.25 g, 41%). 1H NMR (500 MHz, $CDCl_3$): δ 5.14 (dd, $J = 7.1, 1.3$ Hz, 2H), 4.5 (m, 4H, OCH_2), 2.09 (m, 4H, CH_2), 1.9 (m, 6H, CH_3), 1.8 (m, 6H, CH_2), 1.6-1.3 (m, 10H, CH_2), 1.07-0.95 (m, 6H, CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 172, 171, 131.5, 124, 69, 36.8, 35, 29, 25.7, 25.3, 19.2, 17.6; HRMS: m/z ($M+H$)⁺ and ($M+NH_4$)⁺. Calcd for $C_{23}H_{38}ClN_3O_2$: 424.27. Found: 424.27 and 441.3117 (441.311 - 18 = 423.3) respectively.

2,4-Bis((3,7-dimethyloct-6-en-1-yl)oxy)-6 ((trimethylsilyl)ethynyl)-1,3,5-triazine, 3

A mixture of 2-chloro-4,6-bis((3,7-dimethyloct-6-en-1-yl)oxy)-1,3,5-triazine (**2**) (1.2 g, 2.47 mmol), ethynyltrimethylsilane (0.29 g, 2.96 mmol), K_2CO_3 (0.4 g, 2.97 mmol), $Pd(PPh_3)_4$ (0.28 g, 0.24 mmol) and CuI (0.09 g, 0.49 mmol), were dissolved in 10 mL of THF under argon atmosphere then refluxed for 6 hr. (Scheme III). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation, was dried with anhyd. Na_2SO_4 . The solvent was removed under vacuum to give a brown oily material with yield (1.1 g, 81%). HRMS: m/z ($M+H$)⁺ and ($M+Na$)⁺. Calcd for $C_{28}H_{47}N_3O_2Si$: 485.34. Found: 486.33 and 508.32 (508.32 - 23 = 485.32) respectively.



Reagents and conditions: (i) 3,7-Dimethyloct-6-en-1-ol (2 eq), K_2CO_3 , 0-50°C, 6 h, THF, (ii) Trimethylsilyl acetylene, K_2CO_3 , $Pd(PPh_3)_4$, CuI , THF, Reflux.

Scheme III — Synthesis of intermediate compound

1,3,5-Trichloro-2,4,6-triiodobenzene, 5

Periodic acid (3 g, 13.16 mmol) was added slowly to 50 mL of concentrated sulfuric acid and stirred for one hour, then Potassium iodide (6.5 g, 39.49 mmol) was added to the mixture slowly at 0°C. After the reaction reached RT, 1,3,5-trichlorobenzene (**7**) (0.789 g, 4.38 mmol) was added (Scheme IV). The solution was poured into a mixture of ethyl acetate (50 mL) and water (50 mL). The organic layer after separation, was dried with anhyd. Na_2SO_4 . The solvent was removed under vacuum to give solid material with a yield (1.5 g, 62%). m.p. 280°C. HRMS: m/z ($M+H$) and ($M+Na$)⁺. Calcd for $C_3Cl_3I_3$: 557.62. Found: 558.6 and 582.6.

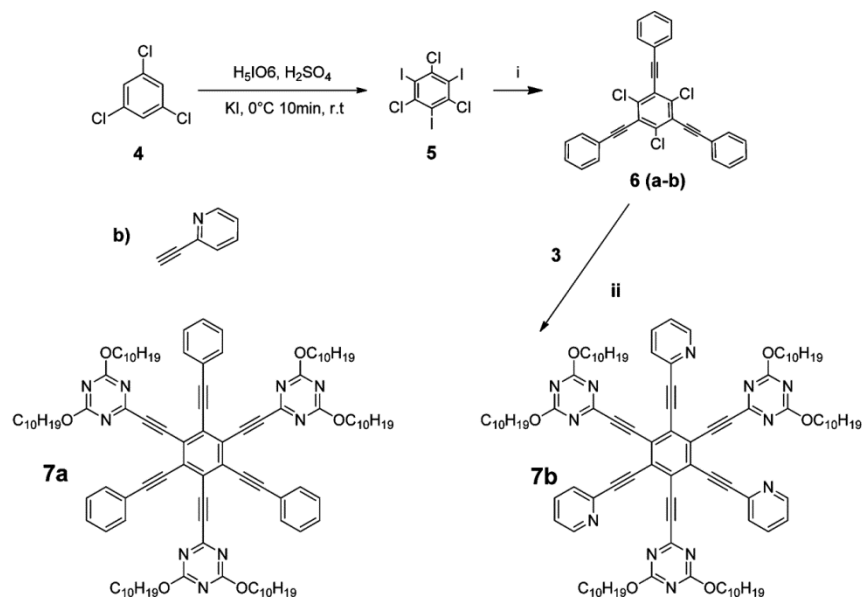
((2,4,6-Trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl) tribenzene, 6a

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**5**) (0.5 g, 0.896 mmol), ethynylbenzene (0.275 g, 2.68 mmol), $Pd(PPh_3)_4$ (0.0102 g, 0.089 mmol), CuI (0.034 g, 0.179 mmol) and Et_3N (0.28 g, 2.86 mmol) were dissolved in 10 mL of dioxane under argon atmosphere then stirred at 75°C for 6 hr (Scheme IV). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation, was dried with anhyd. Na_2SO_4 . The solvent was evaporated under reduced pressure and the crude product purified by column chromatography with hexane/ethyl acetate (5% EtOAc) as an eluent to give white powder with yield (0.35 g, 81%). m.p. 140-145°C.

1H NMR (500 MHz, $CDCl_3$): δ 7.6 (m, 6H, Ar-H), 7.4 (m, 9H, Ar-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ 142, 132.5, 129.2, 128.5, 121.8, 81.6, 74; HRMS: m/z ($M+H$)⁺ and ($M+Na$)⁺. Calcd for $C_{30}H_{15}Cl_3$: 481.80. Found: 483.02 and 505.0219 respectively.

2,2',2''-((2,4,6-Trichlorobenzene-1,3,5-triyl) tris(ethyne-2,1-diyl) tripyridine, 6b

A mixture of 1,3,5-trichloro-2,4,6-triiodobenzene (**5**) (0.427 g, 0.765 mmol), 2-ethynylpyridine (0.236 g, 2.29



Reagents and conditions: (i) 2-Ethynylthiophene, Pd(PPh₃)₄ (0.02), CuI (0.04), Et₃N (3.2 eq), Dioxane, 75°C, 6 h, (ii) Pd(PPh₃)₄, CuI, K₂CO₃, Dioxane, 80°C, 16 h.

Scheme IV — Synthesis of six-armed compounds

mmol), Pd(PPh₃)₄ (0.088 g, 0.076 mmol), CuI (0.029 g, 0.153 mmol), Et₃N (0.24 g, 2.44 mmol) were dissolved in 10 mL of dioxane under argon atmosphere then stirred at 75°C for 6 hr (Scheme IV). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation, was dried with anhyd. Na₂SO₄. Under vacuum, the solvent was evaporated and the crude product purified by column chromatography with hexane/ethyl acetate (3% EtOAc) as an eluent to give white powder with yield (0.29 g, 78%). m.p.195-200°C. ¹H NMR (500 MHz, CDCl₃): δ 7.45 (m, 3H), 7.42 (m, 6H), 7.3 (m, 3H); ¹³C NMR (500 MHz, CDCl₃): δ (145.6, 140.8, 134, 133.8, 129.6, 128.69, 128.6, 100.4, 97.9); MS: *m/z* (2M⁺). Calcd for C₂₇H₁₂Cl₃N₃: 483.02. Found: 968.0178.

6,6',6''-((2,4,6-Tris(phenylethynyl)benzene-1,3,5-triyl) tris (ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine), 7a

A mixture of ((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tribenzene (**6a**) (0.15 g, 0.31 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (0.48 g, 0.99 mmol), Pd(PPh₃)₄ (0.035 g, 0.031 mmol), CuI (0.011 g, 0.062 mmol) and K₂CO₃ (0.149 g, 1.08 mmol), were dissolved in 10 mL of dioxane under argon atmosphere then stirred at 80°C for 16 hr (Scheme IV). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after

separation, was dried with anhyd. Na₂SO₄. The solvent was evaporated under reduced pressure and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to give oily light brown material with yield (0.37 g, 74%). ¹H NMR: δ 7.36 (m, 9H, Ar-H), 7.2 (m, 6H, Ar-H), 4.8 (s, 6H), 4.2 (t, 12H, OCH₂), 1.9 (m, 12H, CH₂), 1.74 (m, 18H, CH₃), 1.5-1.3 (m, 12H, CH₂), 1.1-0.88 (m, 36H, CH₂), 0.7 (m, 18H, CH₃); ¹³C NMR (126 MHz, CDCl₃): δ 172.5, 170.9, 133, 131.8, 129.7, 128.9, 125.1, 125.08, 122.3, 88.5, 86.45, 82, 74.4, 66.8, 42.8, 42.5, 37.7, 37.5, 36.4, 36.3, 30.22, 29.9, 29.4, 26.2, 25.9, 20.02, 19.9, 18.3, 13.7, 13.5, 13.25, 13.23; FT-IR (KBr): 2969, 2919, 2853, 1748, 1566, 1525, 1495, 1460, 1431, 1410, 1303 cm⁻¹; MS: *m/z* (M+3H)⁺ and (M+3Na)⁺. Calcd for C₁₀₅H₁₂₉N₉O₆: 1612.01. Found: 538.34 and 560.67 respectively.

6,6',6''-((2,4,6-Tris(pyridin-2-ylethynyl) benzene-1,3,5-triyl) tris(ethyne-2,1-diyl)) tris(2,4-bis((3,7-dimethyloct-6-en-1-yl) oxy)-1,3,5-triazine), 7b

A mixture of 2,2',2''-((2,4,6-trichlorobenzene-1,3,5-triyl)tris(ethyne-2,1-diyl))tripyridine (**6b**) (0.12 g, 0.248 mmol), Pd(PPh₃)₄ (0.028 g, 0.024 mmol), 2,4-bis((3,7-dimethyloct-6-en-1-yl)oxy)-6-((trimethylsilyl)ethynyl)-1,3,5-triazine (**3**) (0.36 g, 0.74 mmol), CuI (0.009 g, 0.04 mmol) and K₂CO₃ (0.12 g, 0.868 mmol), were dissolve in 10 mL of dioxane under argon atmosphere then stirred at 80°C for 16 hr

(Scheme IV). The solution was poured into a mixture of ethyl acetate (20 mL) and water (20 mL). The organic layer after separation, was dried with anhyd. Na_2SO_4 . The solvent was evaporated under reduced pressure and the crude product purified by column chromatography with hexane/ethyl acetate (2.5% EtOAc) as an eluent to give light brown oil with yield (0.25 g, 62%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.58 (m, 3H, Ar-H), 7.4 (m, 3H, Ar-H), 7.22 (m, 6H, Ar-H), 4.9 (s, 6H), 4.23 (t, 12H, OCH_2), 1.84 (m, 18H, CH_2), 1.66 (m, 18H, CH_3), 1.5- 1.3 (m, 12H, CH_2), 1.25 – 0.86 (m, 36H, CH_2), 0.78 (m, 18H, CH_3); $^{13}\text{C NMR}$: δ 171.7, 171.2, 142.5, 137.5, 136.2, 132.05, 131.14, 127.9, 124.7, 123.6, 121.9, 99.5, 99.3, 82, 67, 41.3, 41.1, 37.2, 35.9, 31.9, 29.6, 29.4, 25.7, 25.4, 22.62, 19.5, 17.6, 14.12, 13.5, 13.19; FT-IR (KBr): 2966, 2925, 2853, 1732, 1566, 1521, 1501, 1458, 1430, 1411, 1374 cm^{-1} ; HRMS: m/z : (M+3Na) $^{+3}$. Calcd for $\text{C}_{102}\text{H}_{126}\text{N}_{12}\text{O}_6$: 1616. Found: 561.98.

4-(Dodecyloxy) benzoic acid (4-DBA), 8

A mixture of 4-hydroxy benzoic acid (8.2 mmol), 1-bromododecane (5.5 mL, 23 mmol, 2.8 eq) and KOH (1.3 g, 23 mmol, 2.8 eq) were dissolved in (25 mL) of ethanol and refluxed for two days (Scheme II). The mixture was hydrolysed by adding 10% aqueous KOH (12 mL) and refluxed overnight. After cooling down, the reaction mixture was acidified with HCl (6 M), the precipitate filtered, washed with water and recrystallized from ethanol to obtain the pure product 4-dodecyloxybenzoic acid as white solid material with yield (4.55 g, 91%). $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 8.10 (d, 2H), 6.98 (d, 2H), 4.07 (t, 2H), 1.84 (m, 2H), 1.48 (m, 2H), 1.37-1.28 (m, 16H), 0.91 (t, 3H); FT-IR (KBr): 2914, 2848, 2559, 1670, 1604 cm^{-1} .

Organic salt, 9a: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.92 (d, 2H), 7.4 (d, 6H, Ar-H), 7.24 (m, 9H, Ar-H), 6.8 (d, 2H, Ar-H), 4.97 (s, 6H), 4.2 (t, 12H, OCH_2), 3.8 (t, 2H, OCH_2), 1.78 (t, 18H, CH_3), 1.6-1.3 (m, 24H, CH_2), 1.1- 0.9 (m, 60H, CH_2), 0.78 (m, 18H, CH_3); $^{13}\text{C NMR}$: δ 171.7, 170, 165, 163, 132.5, 132.3, 131.3, 131.2, 129, 128, 124, 121.7, 121.3, 114.18, 81.5, 73.8, 68, 66, 42, 41.2, 37.3, 35.6, 32.4, 30.2, 31, 29.9, 29.8, 29.5, 28.8, 26.3, 25.8, 23.3, 22, 19.8, 18.1, 17, 14.6, 12; FT-IR (KBr): 2916, 2846, 1674, 1603, 1522, 1503, 1459, 1425, 1362, 1335; HRMS: m/z (M + 3K) $^{+3}$. Calcd for $\text{C}_{124}\text{H}_{159}\text{N}_9\text{O}_9$: 1918.23. Found: 678.7.

Organic salt, 9b: $^1\text{H NMR}$ (500 MHz, CDCl_3): δ 7.9 (d, 2H, Ar-H), 7.58 (m, 6H), 7.4 (m, 3H), 7.22 (m,

3H), 6.75 (d, 2H, Ar-H), 4.9 (s, 6H), 4.2 (t, 12H, OCH_2), 3.75 (t, 2H, OCH_2), 1.78 (t, 18H, CH_3), 1.6-1.3 (m, 24H, CH_2), 1.1- 0.9 (m, 60H, CH_2), 0.78 (m, 18H, CH_3); FT-IR (KBr): 2923, 2852, 1736, 1567, 1521, 1501, 1458, 1431; HRMS: m/z (M+3K) $^{+3}$. Calcd for $\text{C}_{121}\text{H}_{156}\text{N}_{12}\text{O}_9$: 1921.21. Found: 680.36 and 679.7.

Conclusion

We have efficiently synthesized new six armed compounds based on hexa-ethynylbenzenes substituted with different aromatic compounds using 2,4,6-trichloro-1,3,5-triazine and 1,3,5-trichlorobenzene in the presence of palladium catalyst through cross coupling. The pure compounds and organic salt which made between the π -conjugated system and 4-dodecyloxy benzoic acid were investigated by optical polarizing microscope (PM), differential scanning calorimetry (DSC) and spectroscopic analyses ($^{13}\text{C NMR}$, $^1\text{H NMR}$ and HRMS). The compounds showed no liquid crystal behavior.

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References

- Goodby J W, *Liquid Crystals*, 38(11-12) (2011) 1363. <https://doi.org/10.1080/02678292.2011.614700>.
- Cowling S J, Buchkremer A & Goodby J W, *Liquid Crystals*, 38(8) (2011) 1057. <https://doi.org/10.1080/02678292.2011.594526>.
- Lee C-H & Yamamoto T, *Tetrahedron Lett*, 42(24) (2001) 3993. [https://doi.org/10.1016/S0040-4039\(01\)00640-2](https://doi.org/10.1016/S0040-4039(01)00640-2).
- Praefcke K, Kohne B, Singer D, Demus D, Pelzl G & Diele S, *Liquid Crystals*, 7(4) (1990) 589. <https://doi.org/10.1080/02678299008033835>.
- Kondo K, Yasuda S, Sakaguchi T & Miya M, *J Chem Soc Chem Commun*, 55 (1995). DOI:10.1039/C39950000055.
- Kayser B, Altman J & Beck W, *Chem Eur J*, 5 (1999) 754. DOI. [https://doi.org/10.1002/\(SICI\)1521-3765\(19990201\)5:2%3C754::AID-CHEM754%3E3.0.CO;2-E](https://doi.org/10.1002/(SICI)1521-3765(19990201)5:2%3C754::AID-CHEM754%3E3.0.CO;2-E).
- Mongin O, Hoyler N & Gossauer A, *Eur J Org Chem*, 1193 (2000). DOI. [https://doi.org/10.1002/1099-0690\(200004\)2000:7%3C1193::AID-EJOC1193%3E3.0.CO;2-E](https://doi.org/10.1002/1099-0690(200004)2000:7%3C1193::AID-EJOC1193%3E3.0.CO;2-E).
- (a) Kehoe J M, Kiley J H, English J J, Johnson C A, Petersen R C & Haley M M, *Organic Lett*, 2(7) (2000) 969. DOI. <https://doi.org/10.1021/ol005623w>; (b) Wan W B, Brand S C, Pak J J & Haley M M, *Chem Eur J*, 6(11) (2000) 2044. DOI. [https://doi.org/10.1002/1521-3765\(20000602\)6:11%3C2044::AID-CHEM2044%3E3.0.CO;2-Y](https://doi.org/10.1002/1521-3765(20000602)6:11%3C2044::AID-CHEM2044%3E3.0.CO;2-Y).
- Sonoda M, Inaba A, Itahashi K & Tobe Y, *Organic Lett*, 3(15) (2001) 2419. DOI. <https://doi.org/10.1021/ol016274o>.
- (a) Boger D L, Schaum R P & Garbaccio R M, *J Org Chem*, 63(18) (1998) 6329. DOI. <https://doi.org/10.1021/jo980795g>; (b) Sakya S M, Groskopf K K, Boger D L, *Tetrahedron Lett*,

- 38 (1997) 3805. DOI. [https://doi.org/10.1016/S0040-4039\(97\)00751-X](https://doi.org/10.1016/S0040-4039(97)00751-X); (c) Yang X & Seitz G, *Arch Pharm (Weinheim, Germany)*, 325 (1992) 563. DOI. <https://doi.org/10.1021/ol035312w>.
- 11 Lehmann M, *Chem Eur J*, 15(15) (2009) 3638. DOI. <https://doi.org/10.1002/chem.200802625>
- 12 Pradhan B, Pathak S. K, Gupta R K, Gupta M, Pal S K & Achalkumar A S, *J Mater Chem C*, 4(25) (2016) 6117. <https://pubs.rsc.org/en/content/articlelanding/2016/tc/c6tc01260d/unauth#!divAbstract>.
- 13 Turkcu H N, Ocak H, Gurbuz M U, Cakar F & Bilgin-Eran B, *J Molecular Liquids*, 216 (2016) 209. <https://sci-hub.tw/10.1016/j.molliq.2015.12.070>.
- 14 Ravi Shankar Kumar C, Jha A & Sreehari Sastry S, *J Non-Crystalline Solids*, 356 (2010) 334. DOI. <https://doi.org/10.1016/j.jnoncrysol.2009.11.036>.
- 15 Pisupati S, Kumar P A & Pisipati V G K M, *Liquid Crystals*, 27(5) (2000) 665. DOI: <https://doi.org/10.1080/026782900202525>.