■ **Organic & Supramolecular Chemistry**

Novel Annulated Triphenylene Discotic Liquid Crystals Generated by Pictet-Spengler Cyclization

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Triphenylenes have been frontrunner in discotic liquid crystal-line materials since their discovery. They possess great richness of mesomorphism in them. Chemists have been exploring this potential quite often by some substitutions in the core or periphery of the triphenylene molecule. In this current report, we extended the triphenylene ring system by fusing with nitrogen and studied their mesomorphic and optical properties. Four new compounds are prepared using Pictet-Spengler cyclization of hexaalkoxytriphenylene-1-amine with various aldehydes. All the new compounds are well characterized using spectral and elemental analysis. Their mesomorphic properties are evaluated using polarizing optical microscopy, differential scanning calorimetry and X-ray diffractometry. These derivatives showed columnar hexagonal phase with great promise for further studies.

Introduction

Since the discovery of mesomorphism in benzene-based hexaesters by Chandrasekhar et al.,[1] the development of novel discotic liquid crystalline systems have grown leaps and bounds. The Discotic i.e. disc-shaped liquid crystals mainly comprised of a π-fused central core decorated with aliphatic tails, are known to exhibit various mesomorphic structures.[2,3] These materials generally have two, three, four or six-fold rotational symmetry though a few examples with lesser symmetry, non-planar, non-aromatic core surrounded with plural number of aliphatic chains in the periphery are also documented. The liquid crystalline behavior of these disc-based systems are mainly due to nano-segregation of the two constituents: the face on interaction between the conjugated rigid cores which promotes the crystalline character and the melting of the saturated peripheral alkyl chains which provides the liquid like behavior. Self-healing has been observed to be one of the important aspects of these systems which gets reflected in their arrangement in columns which are easily prone to orientation as well as in getting rid of their structural defects. The expedition of mesophases mainly lies in positions, number and nature of the periphery molten alkyl chains and of course in the nature of the central core. π-π interactions, electrostatic interactions, dispersion forces, dipolar and quadrupolar interactions, etc., are primarily responsible for the mesophase formation.[2–4] The inter column distance is mainly a function of length and number of flexible alkyl chains around the core which is usually about 20–40 Å. This makes the interactions between neighboring molecules in the same column stronger than interactions between neighboring columns, and therefore potential candidates for one dimensional charge migration which is extensively used in semi-conducting applications.[5] The anisotropy of conductivity is observed in these materials where conductivity along the columns has been found to be several orders of magnitude greater than in the perpendicular direction. These polycyclic aromatic systems, considered to be main precursors of graphene, have been of vital importance in various semi-conducting devices.[6] DLCs can be synthesized using various strategies in good yield in simple ways. The modifications of these π systems have been reported to suit for applications in devices.[7] One of the important characteristic of this polycyclic π systems is their supramolecular organization in both solid as well as solution state,[8] these aggregates are very sensitive to different stimuli which makes them suitable candidates for devices.[9] Because of the high stability, discotic liquid crystals are considered as precursors toward novel carbon nano-structures. It is assumed that pyrolysis under restricted conditions may uphold the order existing in the mesophase during the formation of the carbonaceous materials. Novel carbon nano and microstructures are the result of pyrolysis of well-defined discotic molecules in the bulk state.[10]

Triphenylenes have been the "work horses" in the discotic cores reported till now.[11–13] Liquid crystalline triphenylenes are attractive; thanks to their low cost preparation in short time and of course their richness in mesomorphic behavior. The variations reported in triphenylene mainly revolve around substitution in the ring apart from the peripheral tails positions and linking to form dimers, polymers, etc. These modifications have often helped researchers in exploring novel mesogens.[13] Generally, in discotics the size of π conjugated core plays a vital role in the stability of mesophases. The extension of π core can

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improve the compound to be more useful in device applications.[14] Addition of hetero atoms in the π conjugated core can influence the semiconducting behavior of the π system and to some extent their mesomorphic and other properties. This strategy has been extensively used by many research groups around the world by extending the core with available chemical strategies.[15] Recently, our group have used this strategy and synthesized heptazine based discotic system which showed excellent mesomorphic behavior.[16] There are few reports of extension of discotic core in which the modifications of triphenylenes was explored for designing new systems. Extension of triphenylene core have been carried in by cross coupling reactions and ring annulations and these extended cores have been found to display excellent mesomorphism.[17–26] These molecules were found to be acting as an electron acceptor moiety and could be used to design donor acceptor dyads. Incorporation of hetero atoms like sulfur found to have great influence in photophysical properties.[18] Extending triphenylene to coronene which modified the electronic properties and reflected in the device applications has been observed. Triazacoronenes have been synthesized using Pictet-Spengler reaction from triphenylenes in high yield.[27–30] In this report we utilized this strategy of expanding the triphenylene ring by annulating with nitrogen and using benzaldehydes. These annulated triphenylenes have been analyzed for mesomorphism.

Results and Discussion

Synthesis

General procedure for the preparation of all the compounds is given in **Scheme 1**. Compounds **2–6** were synthesized follow-
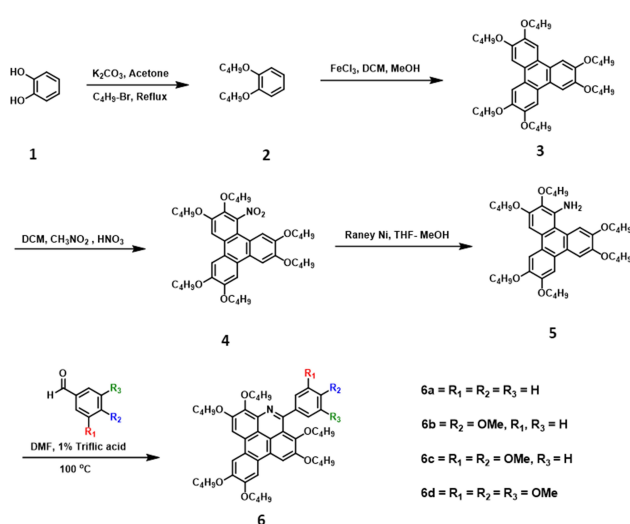
Scheme 1. Synthesis of annulated triphenylene derivatives.

ing the literature procedures.[28,31] Hexabutoxytriphenylene (HAT4) was prepared using Scholl reaction using literature

procedure. The purified HAT4 was mononitrated by using HNO_3. Then the nitro group was reduced to amine using Raney nickel. The isolated amine was used as such for the next step. The Pictet-Spengler reaction was carried out with appropriate aldehyde and amine with triflic acid as catalyst in DMF (**Scheme 1**). The purified product was analyzed for their chemical purity and used for further characterization. The purity of isolated product was confirmed by ^{1}H NMR, ^{13}C NMR, HRMS and elemental analysis (ESI†). The pure compounds were taken for analyzing mesomorphic behavior.

All the compounds were analyzed for their thermal stability using thermogravimetric analysis (TGA). TGA showed that all the compounds have excellent thermal stability (**Figure 1**).
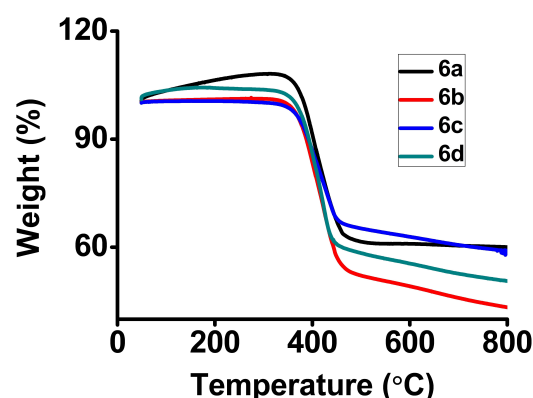
Figure 1. TGA spectra of **6 a, 6 b, 6 c and 6 d** which show good thermal stability of the four compounds.

They were stable till 400 °C which eliminated any thermal decomposition of material during their mesophase characterization.

The samples were viewed in POM under cross polarized conditions. All the compounds were found to be mesomorphic in nature; they displayed mosaic and focal conic textures which are typical indication for columnar mesomorphism (**Figure 2**).

The mesomorphic phase transitions were further confirmed using DSC analysis. DSC thermograms of all the four compounds are given in **Figure 3** and Table 1. Among four

Table 1. Phase transition temperatures (in °C) and enthalpy changes (J g^{-1}) of 6a–6d.

Compound	Heating	Cooling
6a	Cr 78 (36.38) Col$_h$ 149 (10.68) I	I 147(10.13) Col$_h$
6b	Col$_{hp}$ 85 (1.58) Col$_h$ 145(9.56) I	I 143 (9.37) Col$_h$
6c	Cr 139 (41.88) I	I 121 (5.27) Col$_h$
6d	Cr 128 (23.20) I	I 118 (6.97) Col$_h$ 87 (4.24) Cr

compounds, **6 a & 6 b** showed enantiotropic mesophase whereas the compounds **6 c & 6 d** showed monotropic mesophase. The isotropization temperature was found to be decreasing on increasing the number of methoxy group in the peripheral
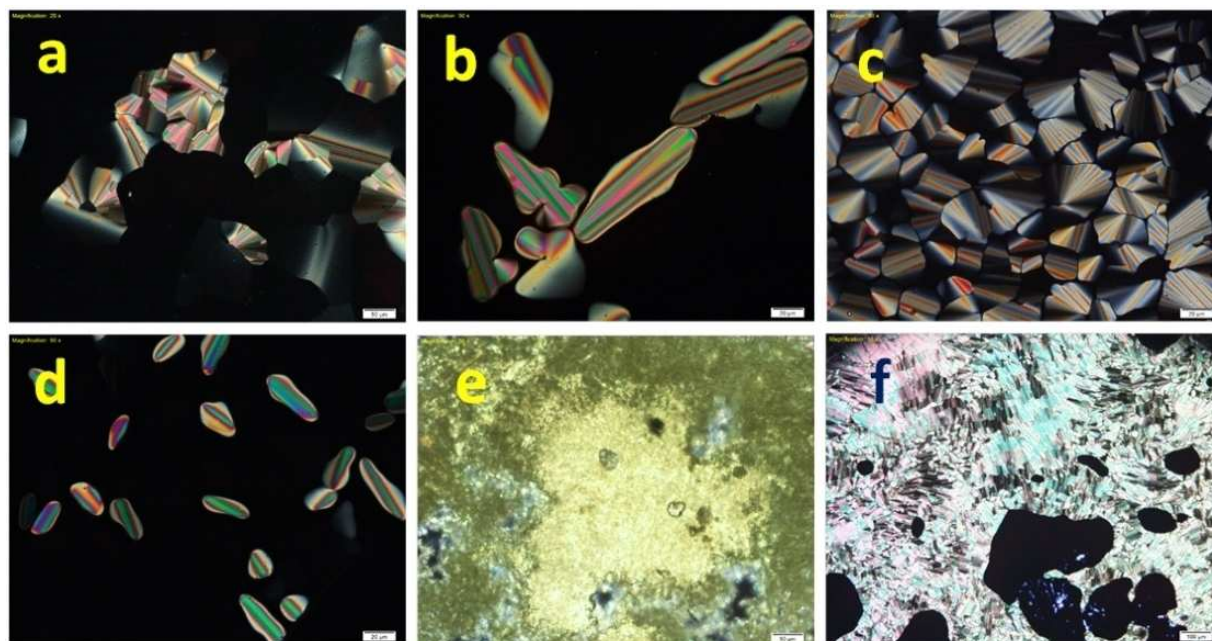
Figure 2. The focal conic and mosaic textures observed under POM for compound a) **6a**; b) **6b**; c) **6c** and d) **6d** upon cooling from the isotropic phase. Texture of col$_{hp}$ phase of compound **6b** (e) at 52 °C; f) at 72°C.
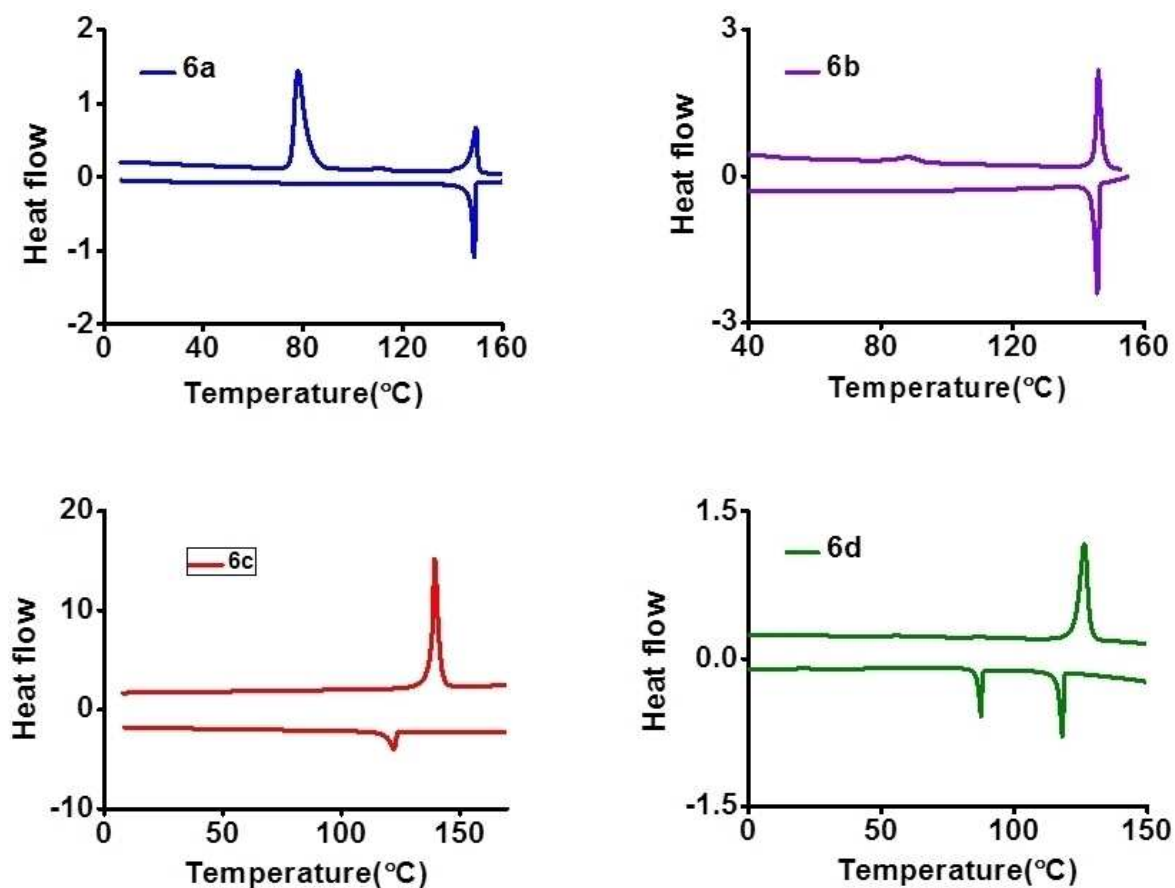

Figure 3. DSC Thermograms of compounds **6a-d**. Showing phase transitions during heating and cooling cycles at a scan rate of 10°C min^{-1}.
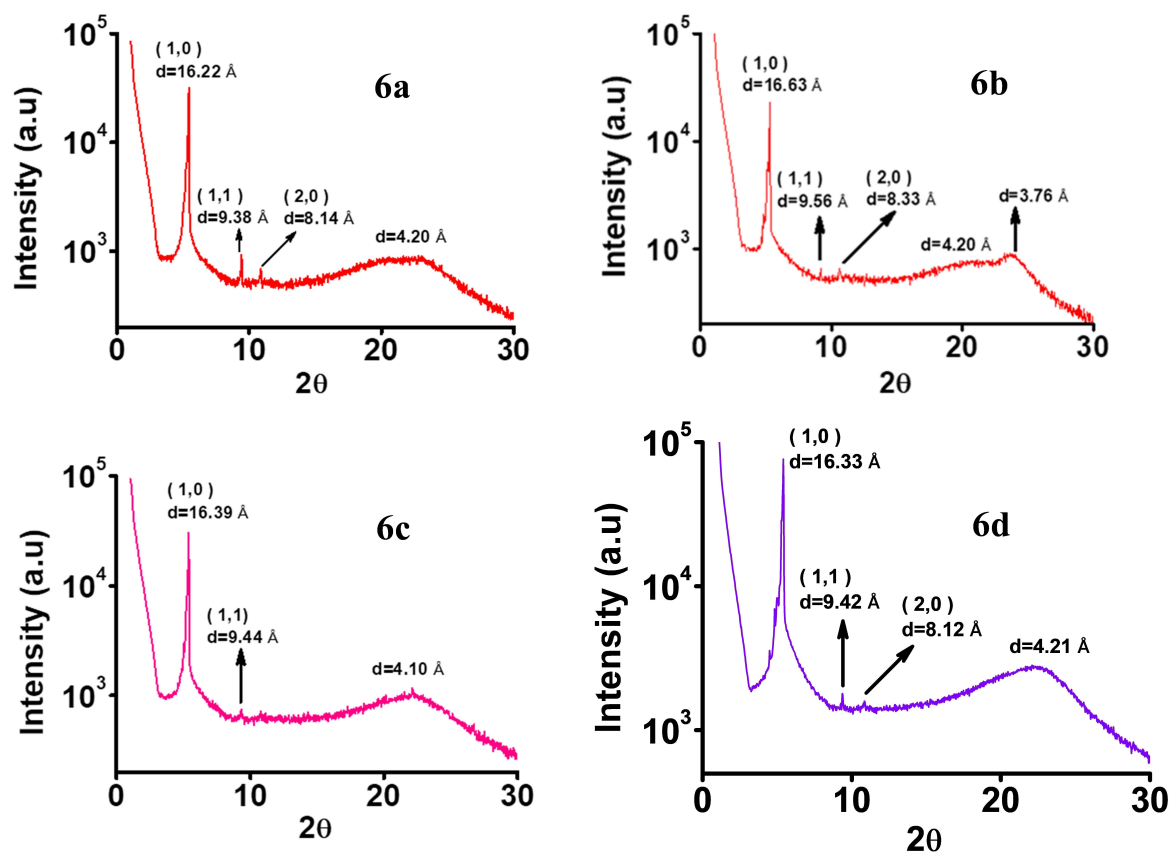
Figure 4. X-Ray diffraction patterns of hexagonal phase of compounds 6a-d

ring. The compound **6c & 6d** were found to be monotropic possibly because of the presence of the extra methoxy group that can hinder the columnar organization. The enthalpy values and POM studies obtained for **6c** and **6d** validates the presence of only melting transitions during heating scan. In the DSC thermogram of compound **6b**, a peak at 85 °C with very low phase transition enthalpy value of 1.58 J g^{-1} was observed. This phase transition was found to be associated with transition from columnar hexagonal to a more ordered columnar hexagonal plastic phase which was further validated from X-ray diffraction studies. POM textures of Col$_{hp}$ phase below its transition temperature is given in **Figure 2e** and **2f**.

Variable temperature X-ray diffraction was carried out in order to further validate the columnar hexagonal phase. The small angle region of the diffraction patterns showed peaks with their spacings in the ratio 1:1/$\sqrt{3}$:1/2 which is typical for a hexagonal lattice and a broad halo corresponding to alkyl chains in the wide angle region (**Figure 4**). On analyzing further, the data showed that the number of molecules occupying a single slice of column was found to be around 1. Apart from the enantiotropic columnar hexagonal phase, compound **6b** was found to exhibit a phase transition associated with very low enthalpy value around 75 °C. While cooling, the above mentioned phase was found to appear slowly (after a few hours). This was confirmed by analyzing the

second heating scan where this small phase transition was absent. The POM and X-ray diffraction studies have been carried out at different temperatures in order to characterize the phase involved. The X-ray diffractogram was recorded for the sample at RT, 50 °C, 70 °C and 85 °C (**Figure 5**). At 70 °C and 85 °C the columnar hexagonal phase was observed. The peaks observed at 70 °C and 85 °C are also seen at 50 °C and room temperature. However, in addition extra reflections were also seen at lower temperatures. We have indexed diffraction patterns at lower temperature assuming that the hexagonal packing of columns remains as in the high temperature phase (ESI). The additional peaks observed at lower temperature are consequences of the presence of an additional periodicity along the column axis; with a periodicity of around 31.56 Å. This also paves the way for explaining the lower enthalpy associated with this phase transition. Similar kind of phase behavior has been reported in the literature[32,33] where this kind of mesophase was termed as columnar plastic phase and was found to be highly ordered compared to the hexagonal phase.

Among all the samples only **6b** showed broader core-core peak around 3.7 Å indicating that the core-core interactions are not very strong. The molecules may be arranged with some staggered conformation which was evident in optimized structures obtained from Gaussian showed in (**Figure 7**). The
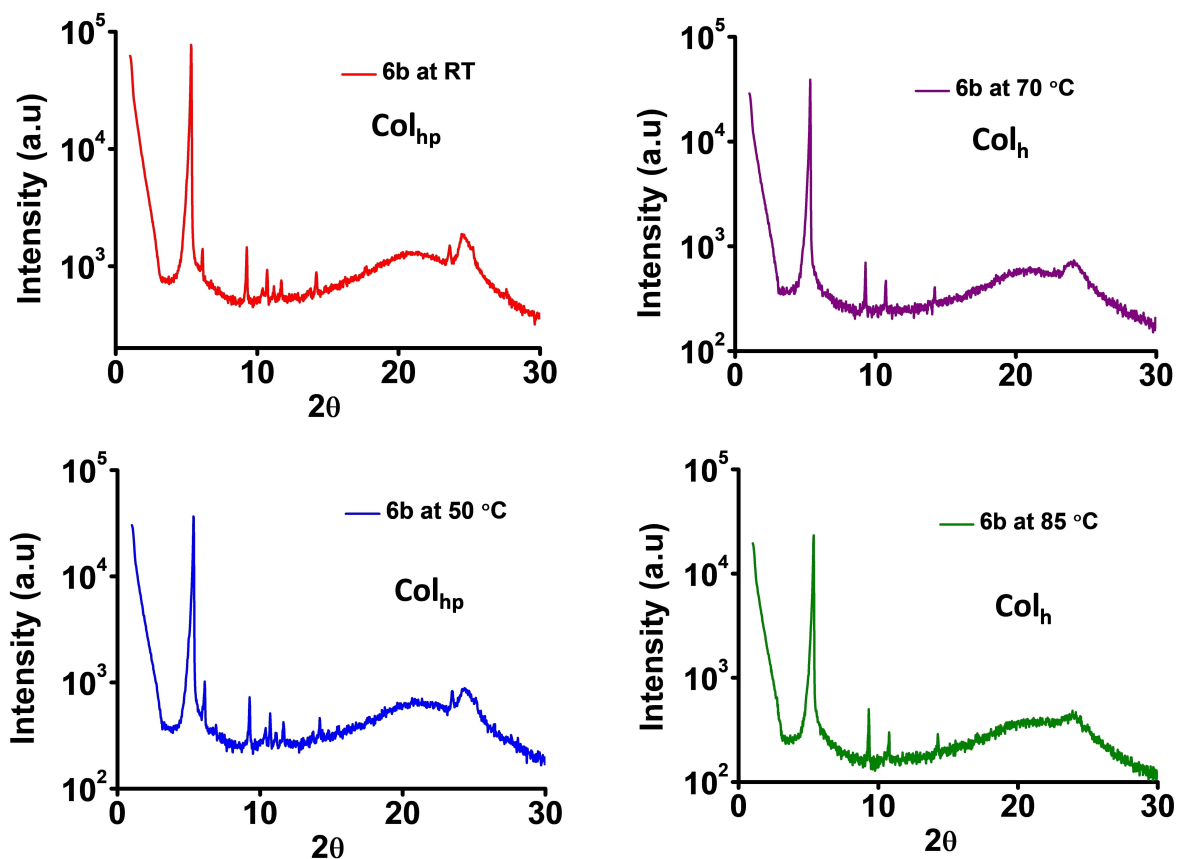
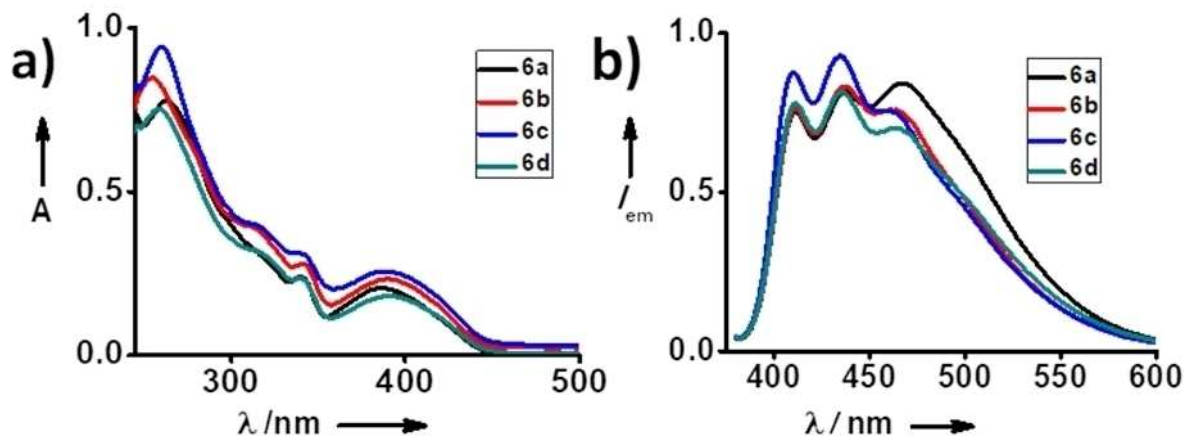**Figure 5.** X ray diffraction pattern of compound 6b at various temperatures

Figure 6. a) Absorption spectra and **b)** emission spectra of compounds **6 a**, **6 b**, **6 c** and **6 d**

optimized structures show peripheral benzene ring is not exactly in plane with the triphenylene ring. The introduction of additional methoxy group in periphery ring further weakens the core-core interactions leading to absence of wide angle peaks. The X-ray data of all compounds are summarized in (**Table 2**).

The samples were analyzed for their optical properties using UV visible absorption spectroscopy and fluorescence spectroscopy in micro molar concentration of chloroform solutions (**Figure 6**). The absorption spectra show four absorption peaks at 254 to 260 nm, 316 nm, 340 nm and 388 nm ($\varepsilon_{370nm} = 1.33 \times 10^{-3} M^{-1} cm^{-1}$ (**6 a**), $1.53 \times 10^{-3} M^{-1} cm^{-1}$ (**6 b**), $1.35 \times 10^{-3} M^{-1} cm^{-1}$ (**6 c**), $1.11 \times 10^{-3} M^{-1} cm^{-1}$ (**6 d**). The emission spectra were recorded in chloroform and all the compounds were excited at 370 nm. The emission spectra of all the compounds looked similar with three intense peaks at
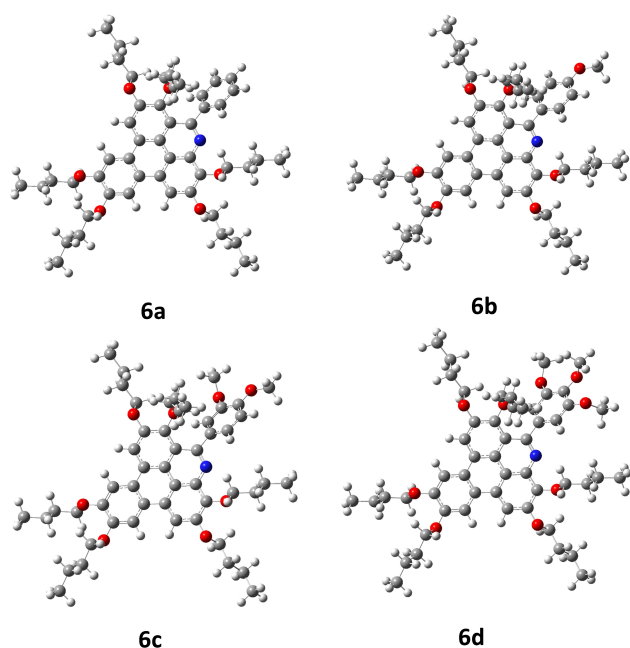
Figure 7. a) Energy-minimized structure of 6a, 6b, 6c, and 6d by using **B3LYP** employing the **6−311G (d p)** basis set.

Table 2. Layer spacing obtained from XRD for **6a, 6b, 6c** and **6d**. ($a =$ lattice parameter $= \sqrt{(4/3)} \times d_{10}$; lattice area $S_h = a^2 \sin 60°$; lattice volume $V_h = a^2 \sin 60° \times h_c$ (h_a if h_c is not observed); No of molecules per slice of column (Z) $= (\sqrt{3} \times N_a \times \rho \times a^2 \times h)/2 M$; $N_a =$ Avogadro number; $\rho =$ Density in Kg/m³; $a =$ lattice parameter; $h_c =$ core core peak (h_a if core core is not observed); M = molecular weight in Kg/m³).

Compound	Phase	d observed	d calculated	Miller indices (h, k)	Parameters
6a	Col$_h$ (120°C)	16.22	16.21	10	a = 18.72 Å
		9.38	9.36	11	S$_h$ = 303.488 Å²
		8.14	8.10	20	V$_h$ = 1274.651 Å³
		4.20(h$_a$)			Z = 1.00
6b	Col$_h$ (80°C)	16.63	16.62	10	a = 19.20 Å
		9.56		11	S$_h$ = 319.251 Å²
			9.6		
		8.33	8.31	20	V$_h$ = 1200.386 Å³
		4.20(h$_a$)			Z = 0.91
		3.76(h$_c$)			
6c	Col$_h$ (120°C)	16.33	16.32	10	a = 18.85 Å
		9.42	9.42	11	S$_h$ = 307.718 Å²
		8.12	8.16	20	V$_h$ = 1295.494 Å³
		4.21(h$_a$)			Z = 0.94
6d	Col$_h$ (120°C)	16.39	16.38	10	a = 18.92 Å
		9.44	9.46	11	S$_h$ = 310.007 Å²
		4.01 (h$_a$)			V$_h$ = 1243.132 Å³
					Z = 0.87

wavelengths of 410 nm, 436 nm, and 465 nm for **6a-d** with high intense peak at around 436 nm for all four compounds. Though multiple peaks in the emission spectra are less common, they have been observed in similar systems.[20,27,30,34] The Stokes shifts between the absorption excitation maxima and emission maxima, of around 66 nm were observed for **6a-d.**

Density functional theory (DFT) studies were done with the help of the GAUSSIAN-09 program with a Becke's three-parameter functional and Lee, Yang and Parr correlation functional (DFTB3LYP) by using the 6−311G (d, p) basis set. (**Figure 7**) Shows the energy minimized structures of **6a - 6d**. The obtained energy gap after analysis was around 3.5 eV. The optical energy gap (E_g) in eV was calculated to be 2.7 eV (according to the equation $E_g = 1240/\lambda_{onset}$, where λ_{onset} was obtained by intersection of the extrapolated tangent of the longest wavelength absorption peak and the x-axis).[16] The optimized structures and HOMO, LUMO Molecular orbitals are given in (**Figure 8**).

Conclusions

A series of annulated triphenylene derivatives have been synthesized from well-established hexaalkoxytriphenylenes using pictet spingler reaction. These compounds were found to be mesomorphic. They exhibit columnar hexagonal phase which was confirmed by X-ray diffraction, POM and DSC. In addition to the columnar hexagonal, one of the compound was found to show a more ordered columnar plastic phase at lower temperature. The optical studies reveal that these materials can be good potent semiconducting material with appropriate band gap which can be utilized in devices.

Supporting Information Summary

The general methods, experimental procedure, ¹H NMR, ¹³C NMR, HR-MS Mass spectra of all the compounds, POM and Miller indices of Col$_{hp}$ diffraction pattern have been provided in the supporting information.

Conflict of Interest

The authors declare no conflict of interest.

LUMO(-1.71159ev)   LUMO(-1.80792ev)   LUMO(-1.81227ev)   LUMO(-1.83486)

3.174ev   3.546ev   3.540ev   3.579ev

HOMO(-4.88607ev)   HOMO(-5.35411ev)   HOMO(-5.35275ev)   HOMO(-5.41397)
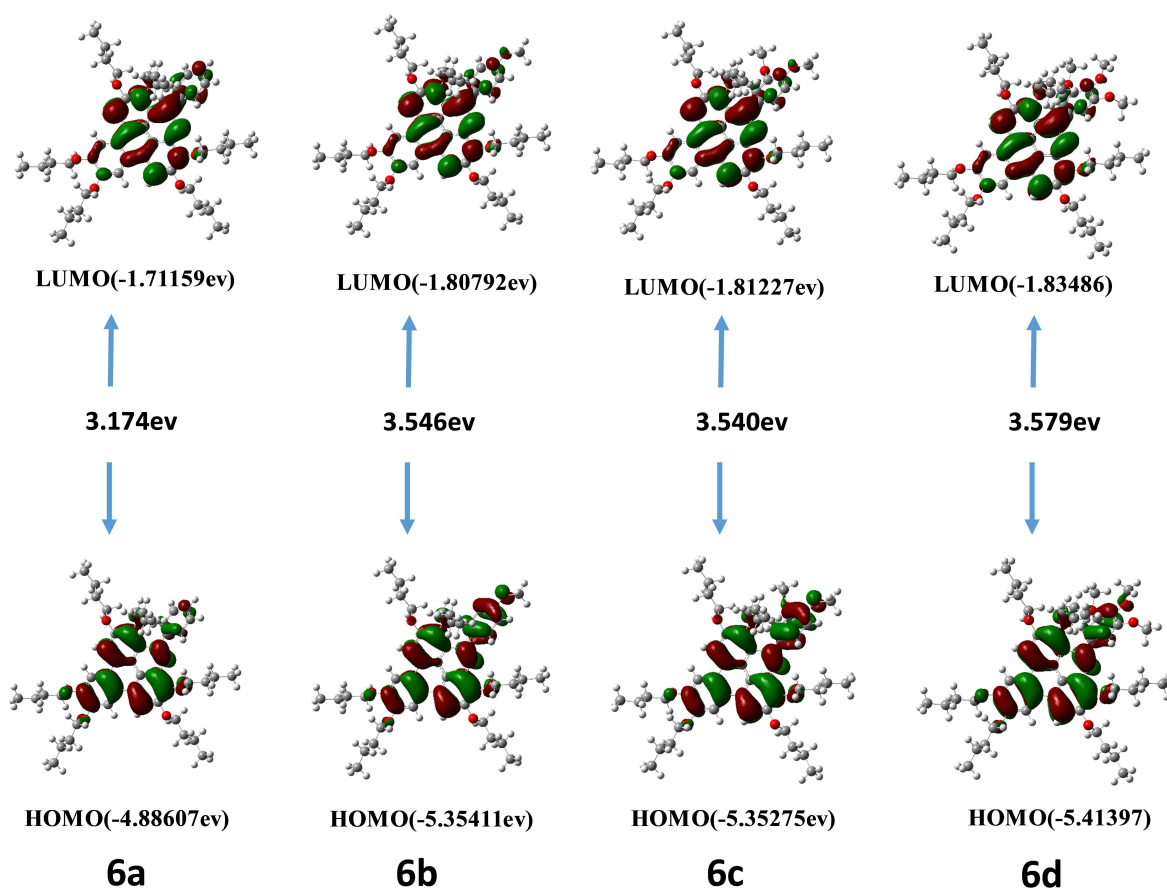
6a   **6b**   **6c**   **6d**

Figure 8. HOMO and LUMO (Energy gap) energy level diagrams of 6a, 6b, 6c and 6d calculated by using **B3LYP** employing the **6−311G (d,p)** basis set.

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