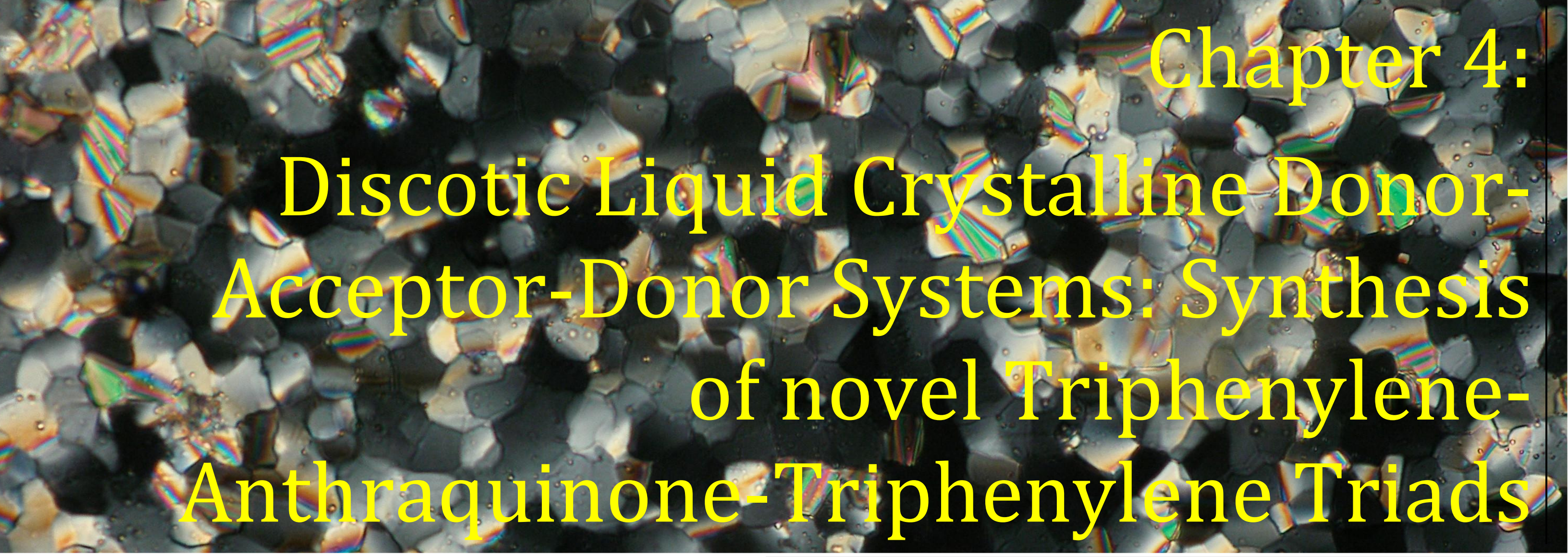
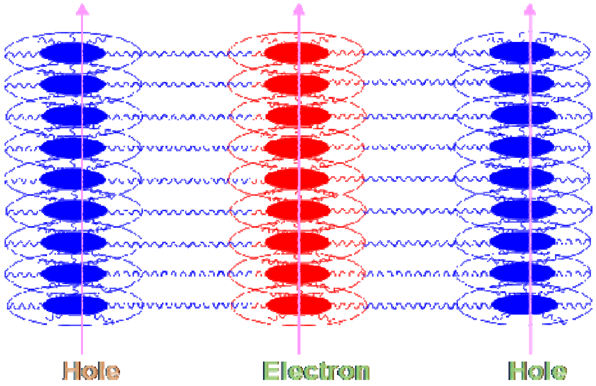
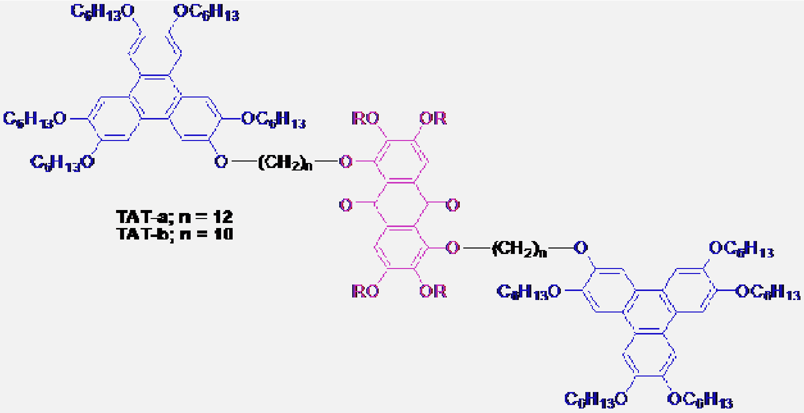
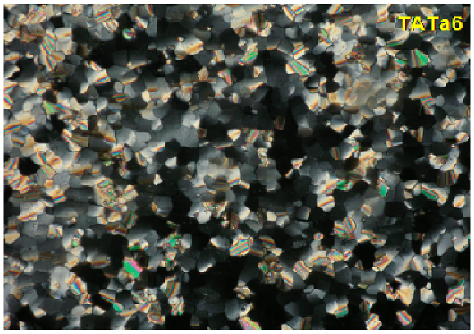
# Chapter 4:

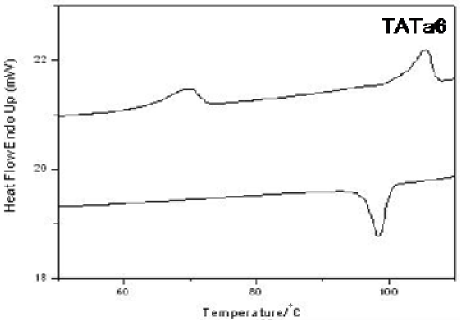
# Discotic Liquid Crystalline Donor-Acceptor-Donor Systems: Synthesis of novel Triphenylene-Anthraquinone-Triphenylene Triads

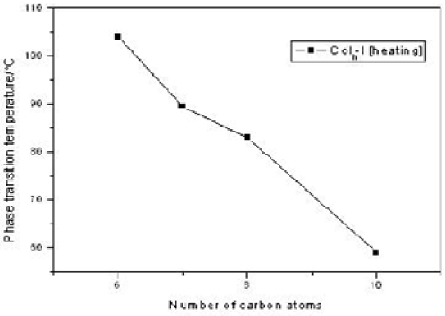


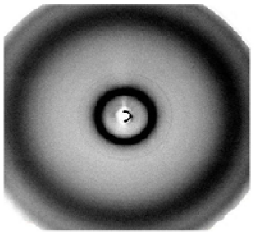


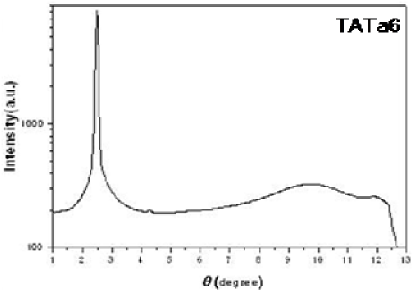


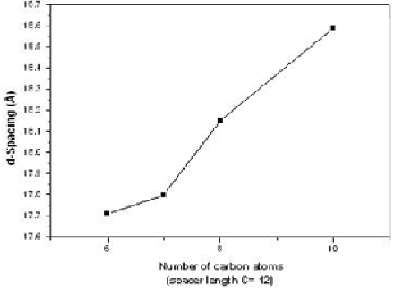


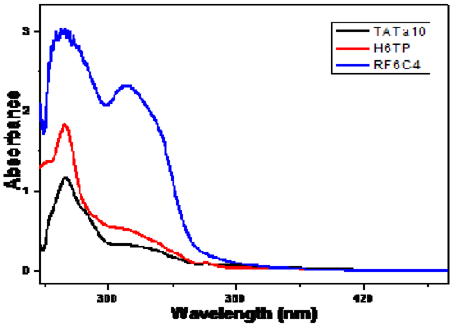


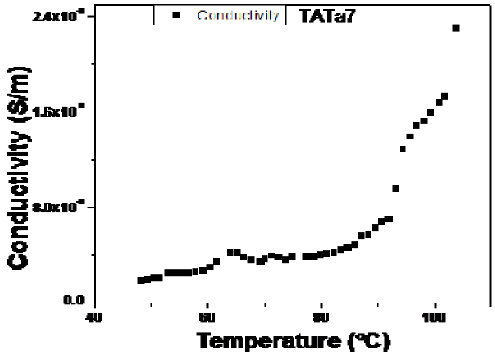












## 4.1. Introduction

The remarkable enhancement in the performance of electronic devices based on organic semiconductors has concerned great attention in recent years.[1] Successful investigations of organic π-conjugated materials have been performed for their application in a number of devices, such as light emitting diodes, solar cells and field effect transistors. The enhanced efficiency of organic devices has origins ranging from proper molecular design to well-defined structured layers essential for effective charge transport.

## 4.2. Rufigallol as a electron deficient discotic core

Rufigallol or 1,2,3,5,6,7-hexahydroxy-9,10-anthraquinone is a derivative of anthraquinone, which can be obtained through the replacement of six aromatic hydrogen atoms of anthraquinone by hydroxyl groups. Rufigallol derivatives are one of the most primitive systems accounted to form columnar mesophases. Elongated core with a 2-fold symmetry axis, coloured in appearance, existence of important polymorphism, thermal stability of the core and fairly easy chemistry of the core make rufigallol fascinating material. Additionally, by the virtue of quinonoid ring in the center, the anthraquinone skeleton is electron-deficient in nature. Quinone belongs to one of the most attractive redox active compounds.[2] Therefore these systems can be doped with electron donor to make n-type

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[1] (a) M. M.- Torrent, C. Rovira, *Chem. Soc. Rev.*, 37, 827, **2008**; (b) H. Alves, A. S. Molinari, H. Xie, A. F. Morpurgo, *Nat. Mater.*, 7, 574, **2008**; (c) L. Zang, Y. Che, J. S. Moore, *Acc. Chem. Res.*, 41, 1596, **2008**; (d) M. Cuccini, *Nature*, 5, 605, **2006**; (e) F. Chen, N. J. Tao, *Acc. Chem. Res.*, 42, 429, **2009**; (f) B. C. Thompson, J. M. J. Frechet, *Angew. Chem. Int. Ed.*, 47, 58, **2008**; (g) E. Menard, M. A. Meitl, Y. Sun, J. -U. Park, D. Jay-Lee, Y. -S. Nam, S. Jeon and J. A. Rogers, *Chem. Rev.*, **107**, 1117, (2007); (h) M. Berggren, D. Nilsson, N. D. Robinson, *Nat. Mater.*, 6, 3, **2007**; (i) N. Koch, *ChemPhysChem*, 8, 1438, **2007**; (j) Y. Sun, Y. Liu, D. Zhu, *J. Mater. Chem.*, 15, 53, **2005**; (k) H. E. Katz, *Chem. Mater.*, 16, 4748, **2004**; (l) S. R. Forrest, *Nature*, 428, 911, **2004**; (m) C. J. Brabec, N. S. Sariciftci, J. C. Hummelen, *Adv. Funct. Mater.*, 11**,** 15, **2001**; (n) C. D. Dimitrakopoulos, P. R. L. Malenfant, *Adv. Mater.*, 14, 99, **2002.**

[2] (a) V. L. Davidson, Ed. *Principles and Applications of Quinoproteins*; Marcel Dekker: NewYork, **1993**; (b) K. E. O'Shea, M. A. Fox, *J. Am. Chem. Soc.,* 113, 611, **1991**; (c) S. Fukuzumi, K. Ohkubo, T. Okamoto, *J. Am. Chem. Soc.* 124, 14147, **2002.**

conductors.[3] The importance of anthraquinone skeleton in liquid crystal field gets significance because of the fact that most of the discotic liquid crystals are made of electron rich (p-type) cores and only a few electron deficient (n-type) discotics are known. A careful literature survey of liquid crystals constructed from discotic compounds reveals that unexpectedly very little work has been focused on rufigallol core. The first synthesis of rufigallol was done by Robiquet[4] in a very poor yield, whereas preparation and purification of this compound was reported by Grimshaw and Haworth. They obtained rufigallol by dehydrative self condensation of gallic acid in the presence of sulphuric acid.[5] The structure of rufigallol was advanced by Klobukowsky.[6] Billard and co-workers reported the first discotic liquid crystalline hexaesters of rufigallol in 1980[7] and since then about more than 100 different discotic liquid crystalline derivatives of this molecule have been prepared and studied for various physical properties.[8,9]

## 4.3. Triphenylene as a electron donor discotic core

Triphenylene is a fully-bezenoid polycyclic aromatic resonance stablized hydrocarbon composed of three fused benzene rings. By the virtue of 18 conjugated π-electrons, the system is electron rich in nature. This is isolated from coal tar. Triphenylene is $C_{3h}$ symmetric, because of which six fold alkyloxy-, alkanoyloxy- or alkylthiol- substituted triphenylene derivatives have been extensively employed as discotic mesogens in liquid crystalline research. Triphenylene derivatives are the representative discotic liquid crystals.[10,11,12] Research into the structure-property relationship of discotic mesomorphic materials has

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[3] V. Khodorkovsky, J. Y. Becker, in *Organic Conductors*, edited by Jean Pierre Farger (New York: Marcel Dekker), Chap. 3.

[4] Robiquet. *Annalen,* 19, 204, **1835.**

[5] J. Grimshaw, R. D. Haworth, *J. Chem. Soc.,* 56, 4225, **1956.**

[6] W. Klobukowsky, *Chem. Ber*., 10, 880, **1877.**

[7] A. Queguiner, A. Zann, J. C. Dubois etal.,in *Liquid Crystals*, edited by Chandrasekhar, , pp.35–40, (Heyden, London, **1980**).

[8] J. Billard, J. C. Dubois, C. Vaucher, etal., *Mol.Cryst.Liq.Cryst.,* 66, 115, **1981**.

[9] S. Kumar, *PhaseTransitions*, 81, 1, 113, **2008.**

[10] S. Kumar, *Liq. Cryst*., 32, 1089, **2005.**

[11] S. Kumar, *Chem. Soc. Rev*., 35, 83, **2006.**

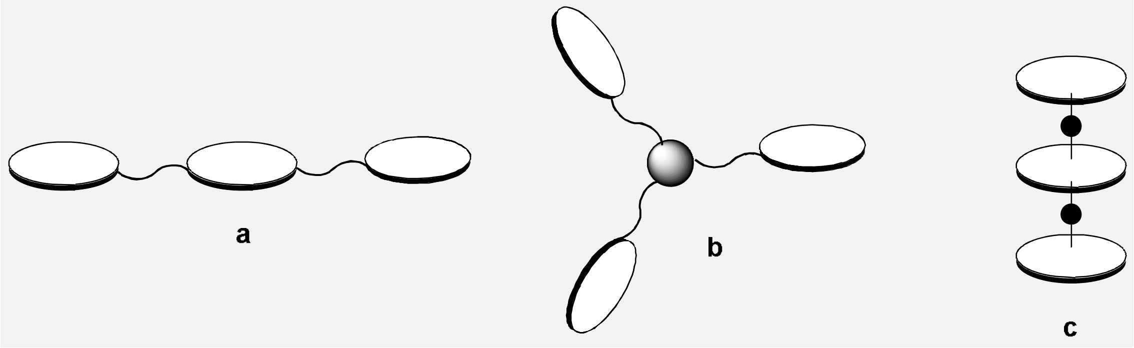
[12] S. Kumar, *Liq. Cryst.,* 31, 1037, **2004.**

largely been focused on triphenylene derivatives. Because of broader mesophase range triphenylenes became privileged as compared to hexa-esters of benzene after their discovery.

The charge and energy migration in triphenylene based discotic liquid crystals have been studied comprehensively and because of these properties, their potential applications in a number of devices have been envisaged. It has recently been demonstrated that the degree of order determines charge mobility in columnar liquid crystalline materials.[13] Columnar discotic molecules have already been used in LEDs where they showed strong reduction of the onset voltage upon perpendicular alignment of the columns.[14]

## 4.4. Discotic trimers

This section deals with mesomorphic properties of trimers made up of discotic molecules. Three types of discotic trimers have been realized; linear **a**, branched (star-shaped) **b**, and metal-bridged triple decker **c**. In a linear trimer, three discotic units are connected with two flexible spacers (Structure **a**); in star-shaped trimer, three discotic fragments are linked to a central non-mesogenic core (Structure **b**), while the triple deckers consist of three discs connected to each other via two central metal atoms (Structure **c**).



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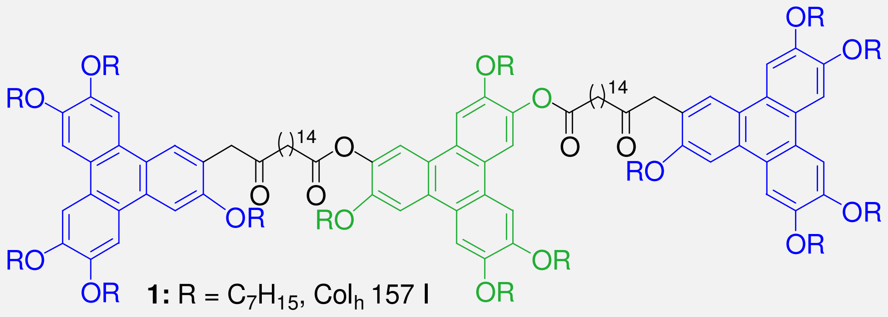
[13] (a) D. Adam, P. Schuhmacher, J. Simmerer, L. Ha ̈ussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer. *Nature*, 371, 141, **1994**; (b) A. M. vande Craats, J. M. Warman, M. P. de Haas, D. Adam, J. Simmerer, D. Haarer, P. Schuhmacher, *Adv. Mater.*, 8, 823, **1996**.

[14] T. Christ, B. Gluesen, A. Greiner, A. Kettner, R. Sander, V. Stuempflen, V. Tsukruk, J. H. Wendorff, *Adv. Mat.*, 9, 48, **1997**.

Since this chapter mainly concerns with the synthesis and characterization of triphenylene-anthraquinone based linear trimers, which are not metal containing, some of the earlier reported discotic linear and star-shaped trimmers are summarized in this section.

Ringsdorf and co-workers prepared a linear triphenylene trimer **1** by reacting a monofunctionalized triphenylene (3,6,7,10,11-pentakis(heptyloxy)-2-triphenylenyl acetate) with an excess of the hexadecanoic diacid and than condensing the resultant acid-functionalized triphenylene derivative with a di-functionalized triphenylene molecule.[15] The trimer is liquid crystalline at room temperature and shows a mesophase to isotropic phase transition at 157 °C. The possibility of a glassy state at low temperature was considered, but the glass transition could not be detected by DSC.



**1:** R = $C_7H_{15}$, $Col_h$ 157 I

A linear trimer **2** in which three triphenylene units were connected *via* ethereal linkage was reported by Boden and co-workers.[16] The compound was prepared by reacting the ω-brominated triphenylene with the 1,2-dihydroxytriphenylene. It shows a complicated thermal behavior. On first heating, it exhibits a crystal to mesophase transition at 60 °C and a mesophase to mesophase transition at 92 °C before going to isotropic melt at 109 °C. On cooling, the columnar mesophase appears at 105 °C that transforms into a glassy state at 32 °C. The glass crystallizes slowly over a period of months.

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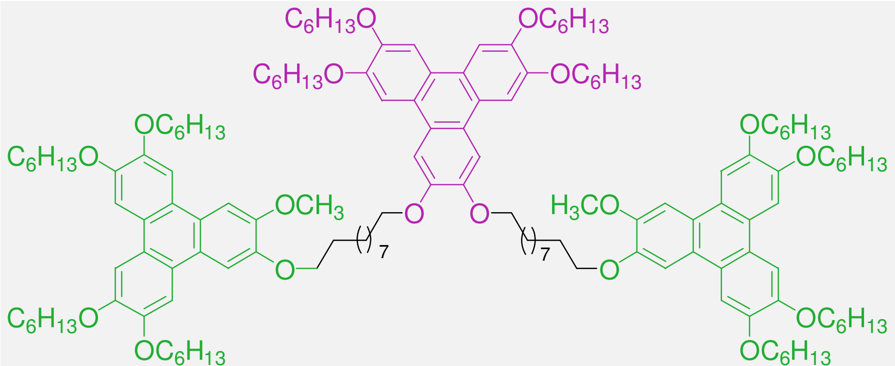
[15] W. Kranig, B. Hüser, H. W. Spiess, W. Kreuder, H. Ringsdorf, H. Zimmermann, *Adv. Mater.,* 2, 36, **1990.**
[16] N. Boden, R. J. Bushby, A. N. Cammidge, P. S. Martin, *J. Mater. Chem*., 5, 1857, **1995.**



**2:** Cr 60 Col 92 $Col_h$ 109 I

The synthesis of star-shaped trimers is relatively easier as it involves the preparation of just monofunctionalized triphenylenes which may be attached to a trifunctional central nucleus to obtain the trimer. Two such trimers have been prepared by Kumar and Manickam.[17] These molecular architectures consist of a trisubstituted benzene as the central core and three triphenylene-based or nitro-functionalized triphenylene-based units as the outer cores. These regional cores are linked to the central core via ester-ether linkages through an alkyl chain spacer. While the nitro-functionalized trimer **3** exhibits a monotropic columnar mesophase, the unfunctionalized trimer **4** was found not to be liquid crystalline. Trimer **3** shows two peaks on first DSC heating run, one weak transition at 161.1 °C and the other broad peak at 181.3 °C. On cooling the columnar phase appeared at 158.7 °C and remains stable to room temperature. By comparision trimer **4** melts at 185 °C and crystallizes at 166 °C on cooling.

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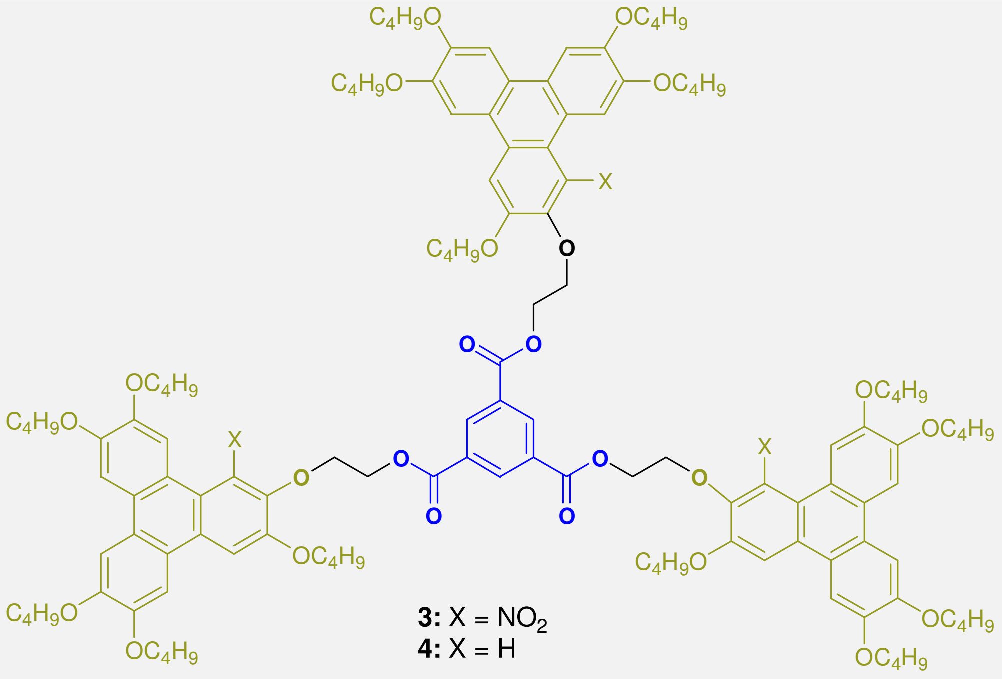
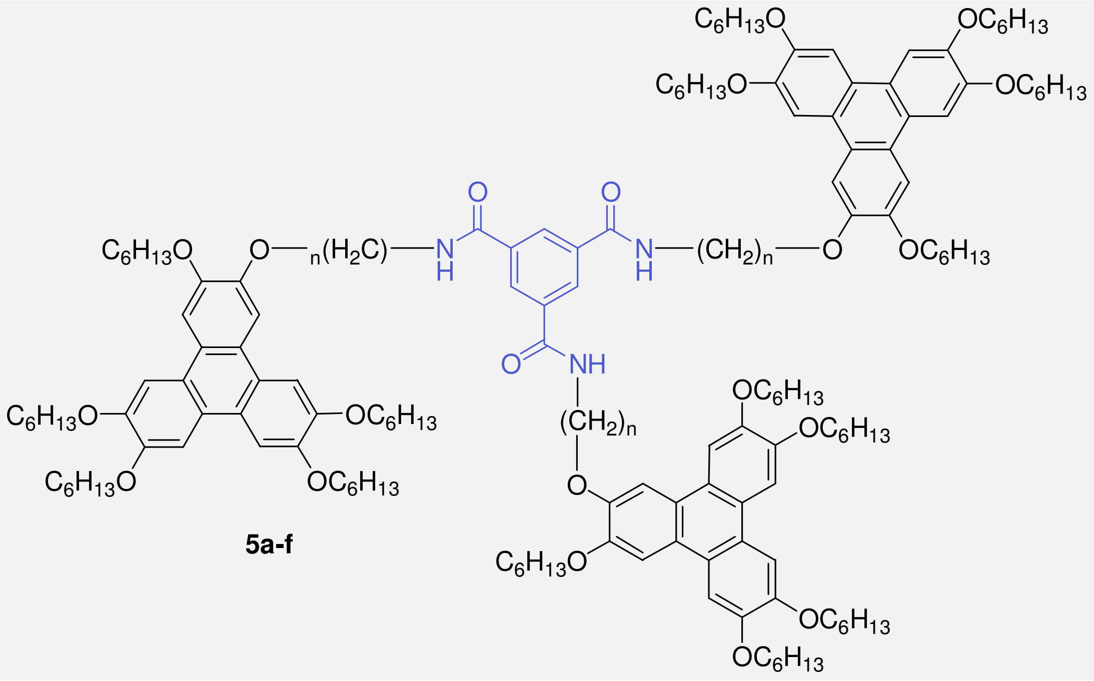
[17] S. Kumar, M. Manickam, *Liq. Cryst.*, 26, 939, **1999.**



**3:** X = $NO_2$
**4:** X = H



**5a-f**

Paraschiv et al. reported a series of 1,3,5-benzenetrisamide derivatives **5a-f** having three hexaalkoxytriphenylene pendent groups.[18,19] These trimers were prepared by reacting an

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[18] I. Paraschiv, M. Giesbers, B. van Lagen, F. C. Grozema, R. D. Abellon, L. D. A. Siebbeles, A. T. M. Marcelis, H. Zuilhof, E. J. R. Sudhölter, *Chem. Mater.*, 18, 4, 968, **2006**.

amino-terminated hexaalkoxytriphenylene with trimesoyl chloride. In these materials, the columnar phase is stabilized via intramolecular hydrogen bonding. This way a high directionality of interaction can be achieved. These materials forms ordered columnar phases in which the charge carrier mobility was several times higher compared to monomeric triphenylene discotics. All compounds exhibit liquid crystalline behavior with high isotropization temperatures due to H-bonding. Interestingly these materials show a variety of columnar phases ($Col_h$, $Col_p$, $Col_{ob}$, $Col_r$ and unidentified Col phases).

Janietz and co-workers prepared a series of star-shaped pentayne-based trimers **6a-d** by coupling a hydroxyl-terminated radial pentaalkynylbenzene derivative with 1,3,5-benzenetricarbonyltrichloride in presence of pyridine and DMAP.[20] All the derivatives exhibited columnar nematic phase. Contrary to its monomeric methyl substituted radial pentayne counterpart, the methyl substituted trimer **6a** displayed monotropic columnar nematic phase. It transforms from the crystalline phase to the isotropic phase at 173.6 °C while heating, but on cooling the mesophase appears at 172.9 °C. The peripheral alkyl chain length has a reciprocal effect on melting as well as clearing temperatures. When cooled from the liquid crystalline phase, the smaller homologues **6a, b** form crystals. On the other hand the mesophase of higher homologues **6c, d** is quenched in to a glassy state on cooling.

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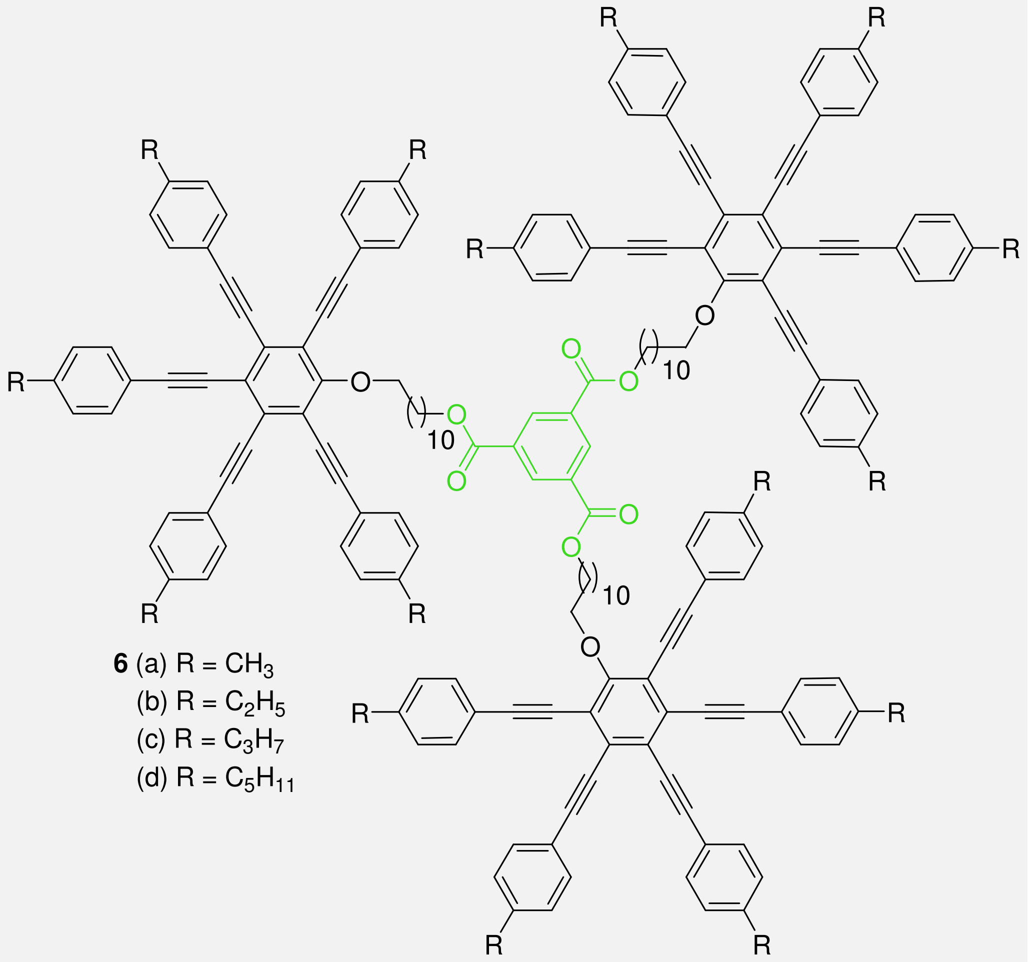
[19] I. Paraschiv, K. de Lange, M. Giesbers, B. van Lagen, F. C. Grozema, R. D. Abellon, L. D. A. Siebbeles, E. J. R. Sudhölter, H. Zuilhof, A. T. M. Marcelis, *J. Mater. Chem.*, 18, 5475, **2008**.

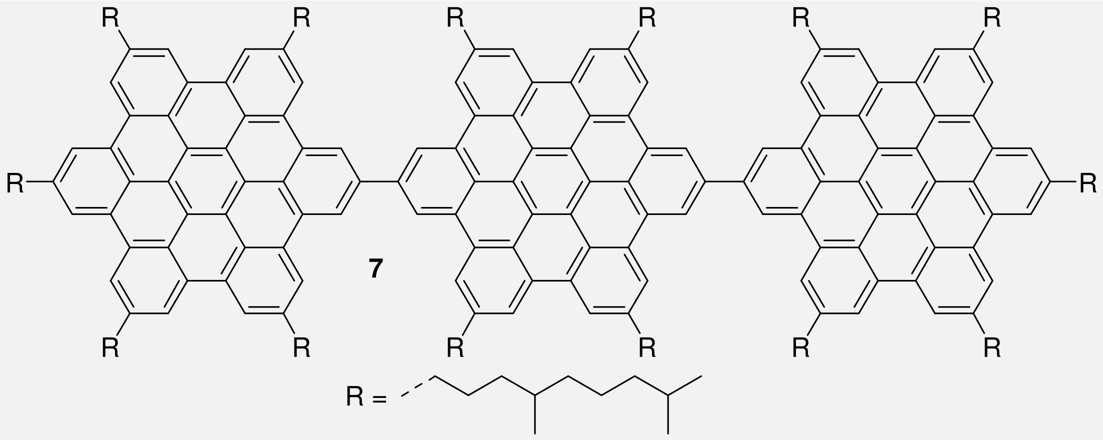
[20] (a) D. Janietz, *Mol. Cryst. Liq. Cryst.*, 396, 251, **2003**; (b) A. Grafe, D. Janietz, *Mol. Cryst. Liq. Cryst.*, 411, 477, **2004**; (c) A. Grafe, D. Janietz, T. Frese, J. H. Wendorff, *Chem. Mater.*, 17, 20, 4979, **2005.**



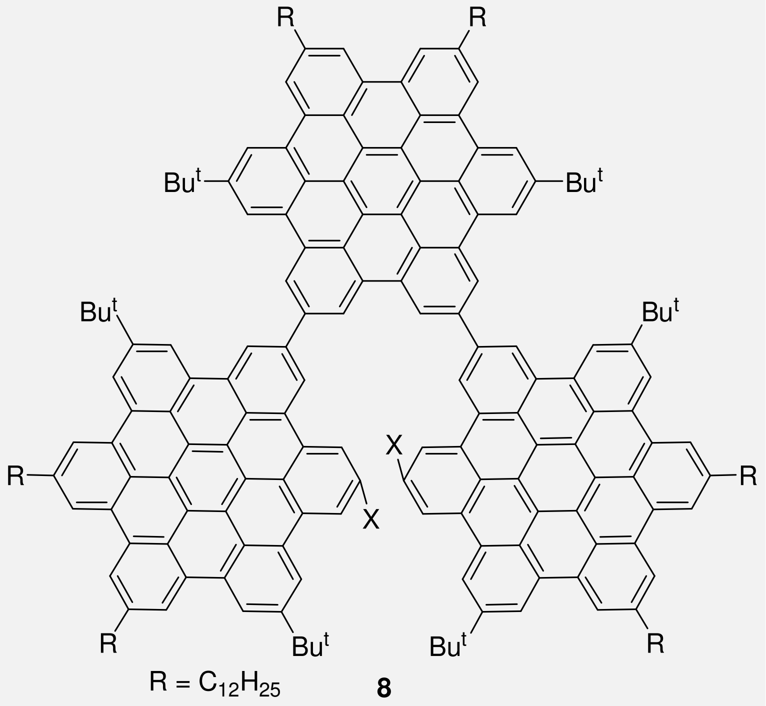
**6** (a) R = $CH_3$
(b) R = $C_2H_5$
(c) R = $C_3H_7$
(d) R = $C_5H_{11}$

Columnar nematic arrangement is stabilized by the combined effect of reduced mobility of pentayne disks within the column due to the star-like covalent linkage and steric repulsion between the long spacer, periphery of the mesogenic core and the bulky benzene connecting group which prevents regular arrangement of the columns into highly ordered lattice. To avoid the steric repulsion, out of plane tilting of pentayne core occurs, which further hinders parallel alignment of columns. On extending the peripheral chain length steric repulsion increases. This consequently results in very small mesophase stability for the pentyl substituted oligomer **6d**. The composites of these oligomers with trinitrofluorenone also displayed columnar nematic mesophase.[20b]

A linear hexabenzocoronene trimer **7** was prepared by Mullen and co-workers.[21] However, the cyclization of **8** to a planar trimer could not be realized due to twisted nature of the former. Because of strong steric hindrance, the intramolecular coupling does not take place. As expected, the ortho-connected HBC trimers **8** do not self-assemble into columnar phase due to twisted conformation, but the linear trimer **7** exhibits a columnar phase. The trimer does not show any transition up to 300 °C but its mesomorphic nature was confirmed by X-ray diffraction studies.



**7**



**8**

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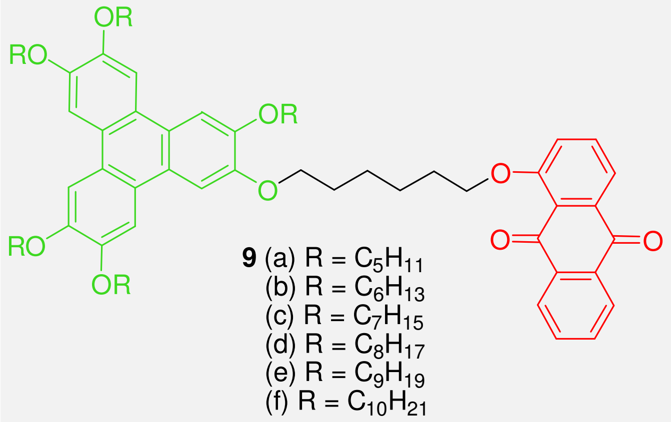
[21] J. Wu, M. D. Watson, N. Tchebotareva, Z. Wang, K. Mullen, *J. Org. Chem.*, 69, 8194, **2004**.

## 4.5. Discotic donor-acceptor systems

One of the most active areas of research in meterial science in recent years has been the search for molecules having both electron acceptor as well as electron donor part in it. The synthesis of a series of triphenylene-anthraquinone dimer **9**, in which the anthraquinone core is not surrounded by any alkyl chain, was reported by Schultz et al.[22] These dimers were obtained by coupling bromine terminated anthraquinone to monohydroxypentaalkoxy triphenylene.



**9** (a) R = $C_5H_{11}$
(b) R = $C_6H_{13}$
(c) R = $C_7H_{15}$
(d) R = $C_8H_{17}$
(e) R = $C_9H_{19}$
(f) R = $C_{10}H_{21}$

The mesomorphic behavior of these materials significantly depends on the peripheral chain length. Whereas **9a-d** did not show liquid crystalline phase, higher homologues **9e-f** displayed an unidentified mesophase. A weak intramolecular charge-transfer interaction in solution between the triphenylene donor and the anthraquinone acceptor was observed by NMR, UV and IR.

Four homologues of triphenylene-anthraquinone based dimers **10a-d** without any peripheral alkyl chain around the acceptor anthraquinone core were prepared by G. Cooke and co-workers.[23] In these dimers the electron rich pentasubstituted triphenylene unit was connected to the electron deficient anthraquinone moiety with the help of methylene spacer having ester linkage towards the anthraquinone end of the spacer. These compounds were

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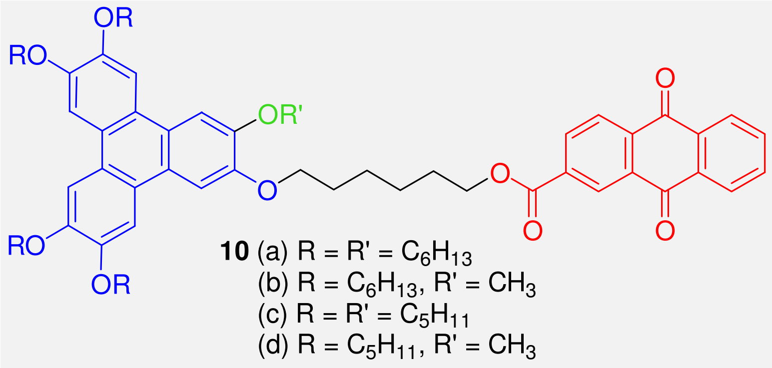
[22] A. Schultz, S. Laschat, A. P. Abbott, M. Langner, T. B. Reeve, *J. Chem. Soc.*, *Perkin Trans. 1*, 3356, **2000**.
[23] G. Cooke, N. Kaushal, N. Boden, R. J. Bushby, Z. Lu, O. Lozman, *Tetrahedron Letters,* 41, 7955, **2000**.

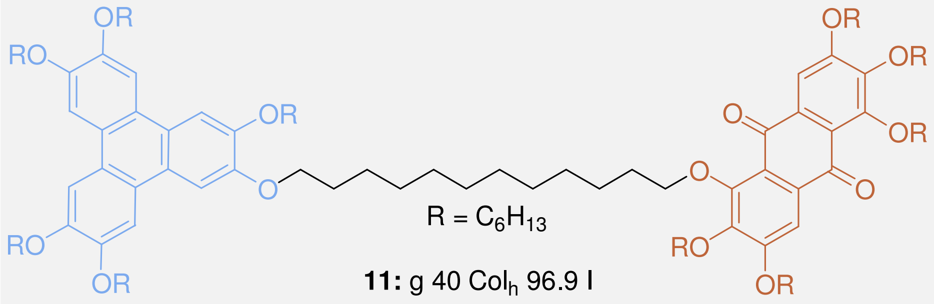
prepared by DCC, DMAP mediated esterification of anthraquinone-2-carboxylic acid with hydroxyl functionalized triphenylene derivative.



**10** (a) R = R' = $C_6H_{13}$
(b) R = $C_6H_{13}$, R' = $CH_3$
(c) R = R' = $C_5H_{11}$
(d) R = $C_5H_{11}$, R' = $CH_3$

The compounds **10a, c** differ from the other two dimers in the sense that in these two derivatives **10a, c** all five peripheral substituent around triphenylene are same. Out of all four dimers, only one **10b** showed a columnar mesophase between temperature range of 89-102 °C. All the other derivatives transformed into isotropic phase either directly or via some other crystalline phase. A recipe of the accurate peripheral alkyl chain length and the presence of smaller methoxy unit on the triphenylene core permits the spacer to accommodate the bulkier moiety in the mesophase structural design and hence encourages the columnar mesophase formation.

Triphenylene-anthraquinone based dimer **11** in which both the electron rich and electron deficient units are surrounded by peripheral alkyl chains was prepared by Kumar et al.[24]



R = $C_6H_{13}$

**11:** g 40 $Col_h$ 96.9 I

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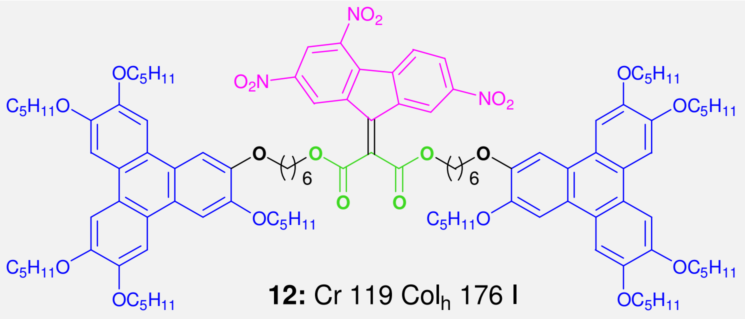
[24] S. Kumar, J. J. Naidu, S. K. Varshney, *Mol. Cryst. Liq. Cryst.,* 411, 355, **2004.**

This material on first heating showed a glass to mesophase transition at 40 °C and this mesophase transformed into isotropic phase at 96.9 °C. On cooling the liquid phase columnar phase appears at 94.3 °C. On subsequent heating, the first transition at 40 °C was not observed and the liquid crystal melted to isotropic liquid.

The stabilization and induction of mesophases due to charge-transfer interactions between donor and acceptor molecules have been well documented.[25] In most of the cases, trinitrofluorenone (TNF) molecule has been used as an electron-acceptor. In order to understand the molecular stacking in liquid crystalline donor-acceptor dimers, TNF molecule has also been covalently connected to the mesogenic moiety.[25,26,27] In a novel triphenylene-based discotic donor-acceptor-donor type dimer, two triphenylene fragments were chemically connected to a TNF molecule.



**12:** Cr 119 $\text{Col}_h$ 176 I

The dimer **12**, a condensation product of the corresponding acceptor diethyl ester and the free alcohol derivative of the corresponding triphenylene, forms columnar mesophase in the temperature range of 119-176 °C. Langmuir-Blodgett film formed by this compound display an edge-on orientation (the columns lie parallel to a solid substrate) of the molecules.[27]

The construction of orthorhombically and hexagonally arranged columns formed by alternate stacking of triphenylene (donor) and TNF (acceptor) has been reported in **13a** and

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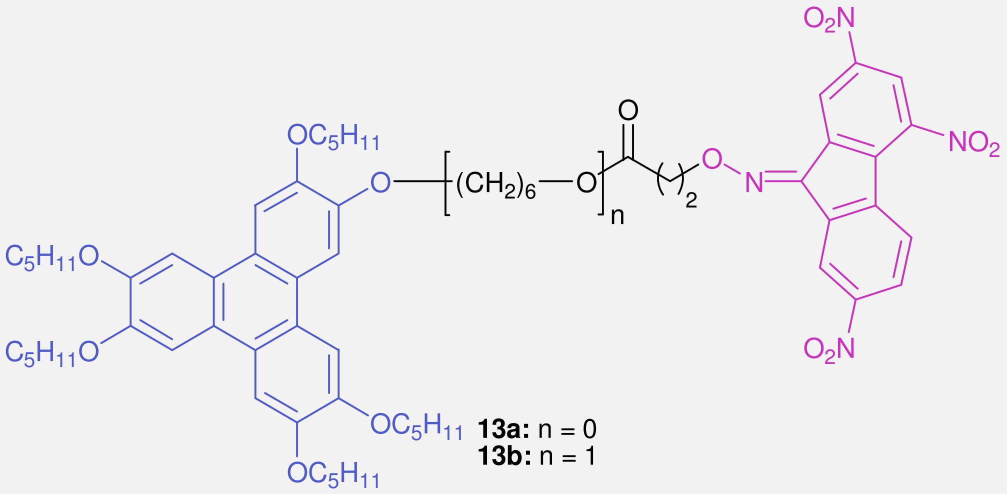
[25] K. Praefcke, D. Singer, in *Hand Book of Liquid Crystals* ed by D. Demus, J. Goodby, G. W. Gray, H.- W. Spiess, V. Vill, Wiley-VCH, Vol. 2B, Chapter XVI, **1998**.

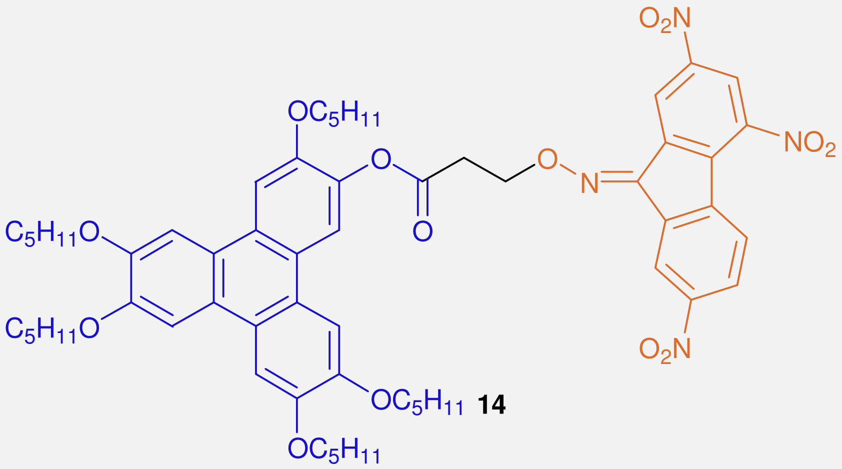
[26] S. Mahlstedt, D. Janietz, A. Stracke, J. H. Wendorff, *Chem. Commun.*, 15, **2000**.

[27] V. V. Tsukruk, H. Bengs, H. Ringsdorf, *Langmuir,* 12, 754, **1996**.

**13b**, respectively. The liquid crystalline phase was stable up to the range of 242-265 °C. On cooling down to room temperature glassy mesophase was obtained.[28]



**13a:** n = 0
**13b:** n = 1



**14**

Similar mesophase behavior was observed in case of **14**.[29] This dimer exhibited stable mesophase behavior between 50 and 265 °C.

## 4.6. Objective

Recently there have been tremendous efforts to achieve both p-type (hole conducting) and n-type (electron conducting) properties in organic semiconducting materials which are

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[28] (a) M. Möller, J. H. Wendorff, M. Wert, H. W. Spiess, H. Bengs, O. Karthaus, H. Ringsdorf, *Liq. Cryst.,* 17, 3, 381, **1994**; (b) M. Möller, V. Tsukruk, J. H. Wendorff, H. Bengs, H. Ringsdorf, *Liq. Cryst.,* 12, 1, 17, **1992**.

[29] D. Markovitsi, H. Bengs, H. Ringsdorf, *J. Chem. Soc., Faraday Trans.*, 88, 1275, **1992**.

crucial for molecular electronics. One elegant approach for such materials is to covalently link electron donor and electron acceptor components at molecular level. These kinds of materials are expected to behave as intrinsic, non-composite p/n-type semiconductors. Such chemical tailoring could lead to the development of other molecular architectures and it is envisaged that the combination of covalent chemistry and molecular self-assembly will be crucial for the development of nano-engineered functional materials for electronic applications.[1] Due to cofacial stacking of aromatic cores, disc-like molecules self assemble into one dimensional columnar wire and these columns in turn self organize themselves in various two-dimensional lattices. The transport along the columnar axis is much faster than between the columns.

Our molecular design is such that it contains the well studied electron rich triphenylene moiety[12] and electron deficient anthraquinone[9] as the hole and electron transporting components, respectively. Stacking of similar core one on the top of other results in formation of molecular wire which may play an important role in design of electronic devices. These molecular double-cables, owing to their incommensurate core sizes, may stack one on top of the other in the columns to give columnar versions of double cable polymers,[30] which could eventually provide side-by-side percolation pathways for electrons and holes in solar cells. Here, we report the synthesis and mesomorphism of novel triphenylene-anthraquinone-triphenylene discotic liquid crystalline symmetric trimers. To the best of our knowledge, these are the first donor-acceptor-donor triads in which all the three components represent discotic mesogenic moiety.

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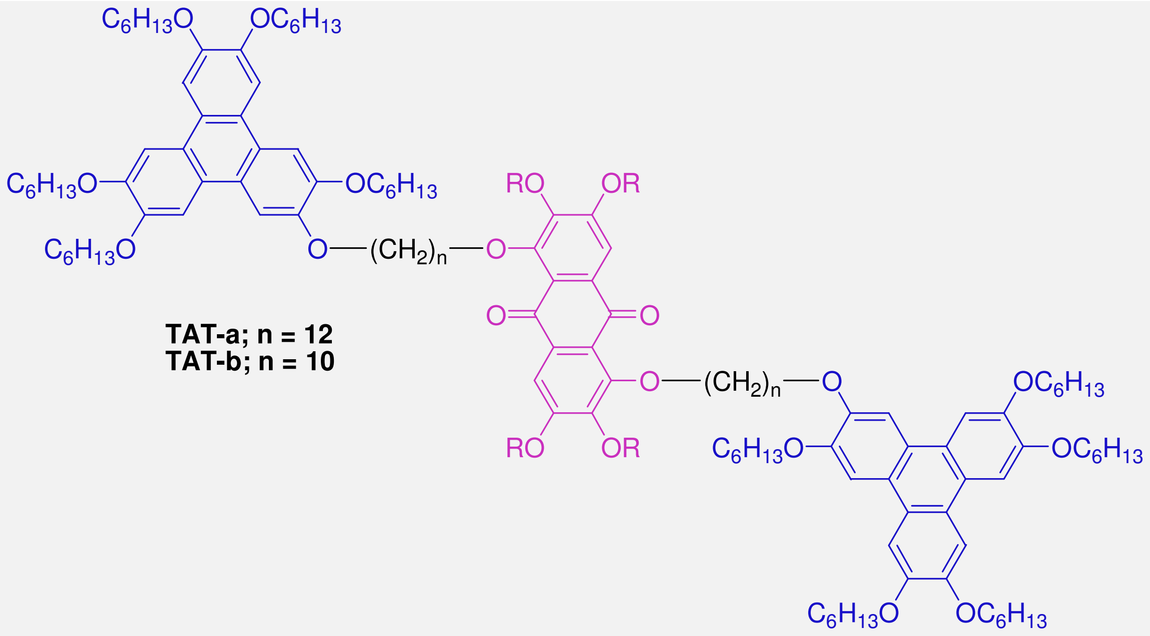
[30] A. Cravino, N. S. Sariciftci, *J. Mater. Chem.*, 12, 1931, **2002**.



## 4.7. Synthesis and Chemistry of rufigallols

Acid-catalyzed dehydration self-condensation of gallic acid **15** yields crude rufigallol **16** which is usually purified through its hexa-acetate **17** (Scheme 1). Recently it was realized that self condensation of gallic acid in presence of $H_2SO_4$ can be performed in high yield by microwave irradiation for about one minute.[31]

Esterification of rufigallol **16** can be done by reacting with an excess of appropriate acid chloride in acetone-pyridine or toluene-pyridine at elevated temperature to yield hexaesters **23**.[7] Two hydroxyl groups can be added at 4 and 8 positions of rufigallol by oxidation in presence of boric acid, yellow mercuric acid in concentrated $H_2SO_4$. Rufigallol is first stirred with boric acid, yellow mercuric acid and concentrated $H_2SO_4$ at room temperature. The resultant mixture can be heated at 250 °C to give octahydroxy-9,10-anthraquinone **21**. Esterification of octahydroxy-9,10-anthraquinone with alkanoyl chlorides affords octa-substituted anthraquinone discotics **22**.[32]

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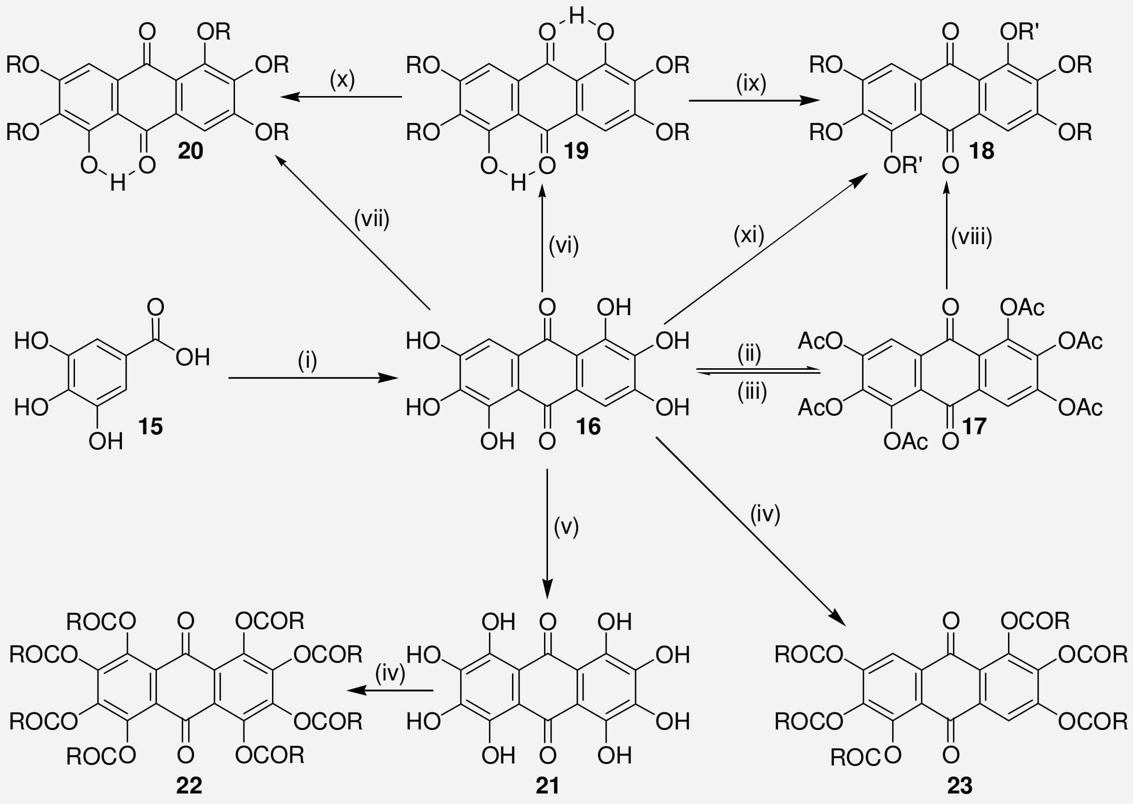
[31] H. K. Bisoyi, S. Kumar, *Tet. Lett.*, 48, 4399, **2007.**

[32] J. Billard, Z. Luz, R. Poupko, *Liq.Cryst.,* 16, 333, **1994.**



**Scheme 1**. (i) $H_2SO_4$, 100 ºC; (ii) $Ac_2O$, $H_2SO_4$; (iii) Aq NaOH; (iv) Py-acetone, RCOCl; (v) $H_3BO_3$, HgO, $H_2SO_4$; (vi) DMSO, NaOH, RBr, TBAB, 80 ºC; (vii) ROH, TPP, DEAD; (viii) DMF, $Na_2CO_3$, RBr, 160 ºC; (ix) DMF, $K_2CO_3$, RBr, TBAB, ~100 ºC; (x) DMF, $Cs_2CO_3$, RBr; (xi) RX, $Cs_2CO_3$, NMP, MW.

The two hydroxyl groups at 1 and 5 positions in rufigallol **16** are hydrogen bonded and therefore, are less reactive. Under mild basic condition 2,3,6,7-substituted tetraethers **19** can be obtained leaving these two hydroxyl groups unreacted. Since most of the tetraethers derivatives of rufigallol are not liquid crystalline, these readily available functional groups at 1 and 5 positions can be easily reacted to achieve liquid crystalline oligomers[33] and main chain polymers.[34] This unequal reactivity also leads to the preparation of several unsymmetrical rufigallol derivatives.[34,35] Tetraethers can be prepared by heating at 80 °C a

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[33] S. K. Gupta, V. A. Raghunathan, S. Kumar, *New J. Chem.*, 33,112, **2009**.

[34] K. S. Raja, V. A. Raghunathan, S. Ramakrishnan, *Macromolecule,* 31, 3807, **1998**.

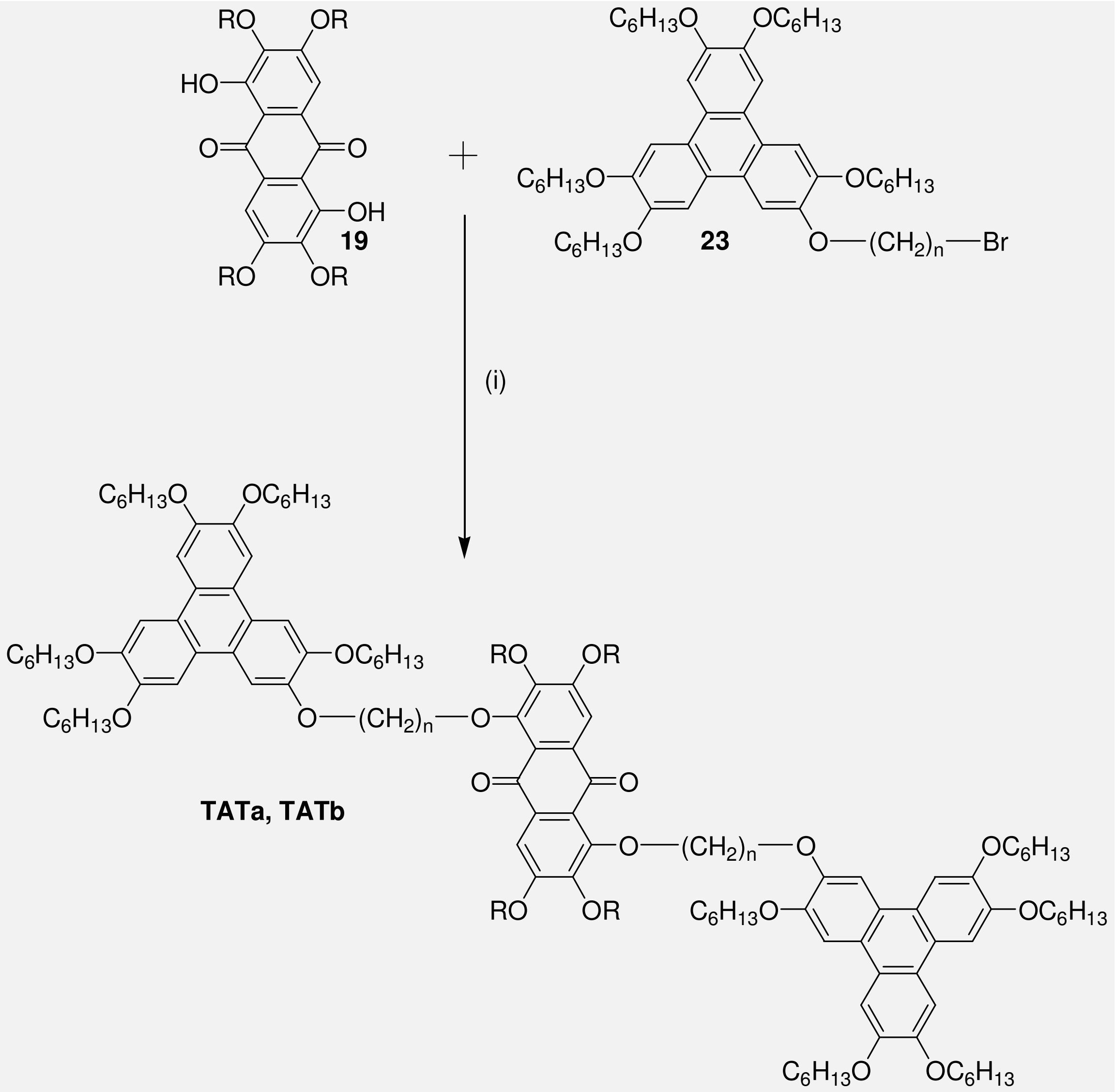
[35] (a) K. S. Raja, S. Ramakrishnan, V. A. Raghunathan, *Chem. Mater.*, 9, 1630, **1997**; (b) R. Y. Dong, C. R. Morcombe, *Liq. Cryst.*, 27, 897, **2000**; (c) Y. Chenard, N. Paiement, Y. Zhao, *Liq. Cryst.*, 27, 459, **2000**; (d) L. Corvazier, Y. Zhao, *Liq. Cryst.*, 27, 137, **2000**; (e) K. Krishnan, V. S. K. Balagurusamy, *Liq. Cryst.*, 27, 991, **2000**.

mixture of rufigallol, appropriate alkyl bromide, sodium hydroxide and tetrabutyl ammonium bromide in dimethyl sulfoxide as a solvent.

Hexaether derivatives **18** can be synthesized by sodium carbonate mediated alkylation of hexaacetate of rufigallol with an excess of appropriate alkyl halide in DMF at reflux temperature. Hexaethers can also be prepared by microwave irradiation of a mixture of rufigallol, alkyl halide and caesium carbonate in NMP as solvent. Tetraethers **19** can also be converted in to hexasubstituted ethers **18** by heating it at 100 °C with a mixture of potassium carbonate, alkyl bromide and tetrabutyl ammonium bromide in dimethyl formamide.

## 4.8. Synthesis of donor-acceptor-donor triads

The synthesis of the novel symmetrical trimers was achieved as shown in Scheme 2. The unequal reactivity of the six phenolic groups of rufigallol **16**, two of which are less reactive by virtue of being intra-molecularly hydrogen bonded to the adjacent quinone carbonyls, was exploited. Etherification of rufigallol **16** under mild conditions produced 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **19** without alkylating the hydrogen bonded C-1 and C-5 positions. These tetraalkoxy derivatives were further alkylated by ω-bromo-substituted triphenylenes **23** with the help of microwave dielectric heating as shown in the Scheme 2, under mild basic conditions to furnish the symmetrical trimers within 10 minutes which is simple, efficient, rapid and economic. All attempts to etherify the intramolecularly hydrogen bonded C-1 and C-5 positions with bulky ω-bromo-substituted triphenylene **23** were failed under classical thermal heating conditions even by using strong basic conditions and prolonged reaction times (24 h). For instance, heating the same reaction mixture in DMF at 100 ºC for 48 h or heating a mixture of **19** and **23** in DMF and NaOH or $K_2CO_3$ for 48 h did not furnish any product.



Scheme 2: Synthesis of triphenylene-anthraquinone triads. (i) $Cs_2CO_3$, NMP, MW. **TATa** Series (n = 12): OR = H (**TATa0**); R = n-$C_6H_{13}$ (**TATa6**); R = n-$C_7H_{15}$ (**TATa7**); R = n-$C_8H_{17}$ (**TATa8**); R = n-$C_{10}H_{21}$ (**TATa10**); R = 3,7-dimethyloctyl (**TATa10'**); R = n-$C_{14}H_{29}$ (**TATa14**); **TATb** Series (n = 10): R = n-$C_6H_{13}$ (**TATb6**); R = n-$C_7H_{15}$ (**TATb7**); R = n-$C_{10}H_{21}$ (**TATb10**); R = 3,7-dimethyloctyl (**TATb10'**); R = n-$C_{12}H_{25}$ (**TATb12**); R = n-$C_{14}H_{29}$ (**TATb14**).

## 4.8.1. Characterization of donor-acceptor-donor triads

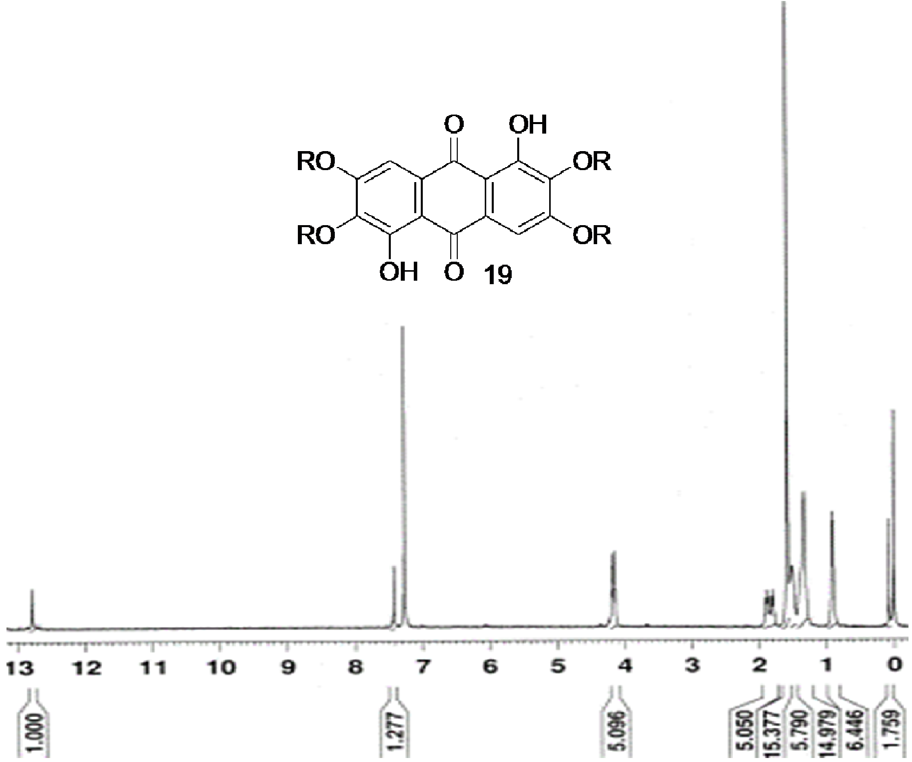


**Figure 1**. $^1$H NMR spectrum of the compound **19**.

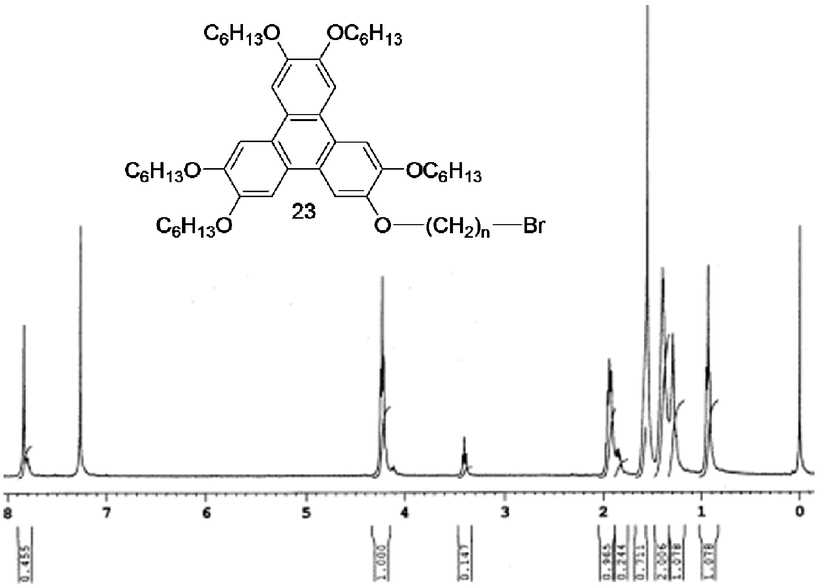


**Figure 2**. $^1$H NMR spectrum of the compound **23**.

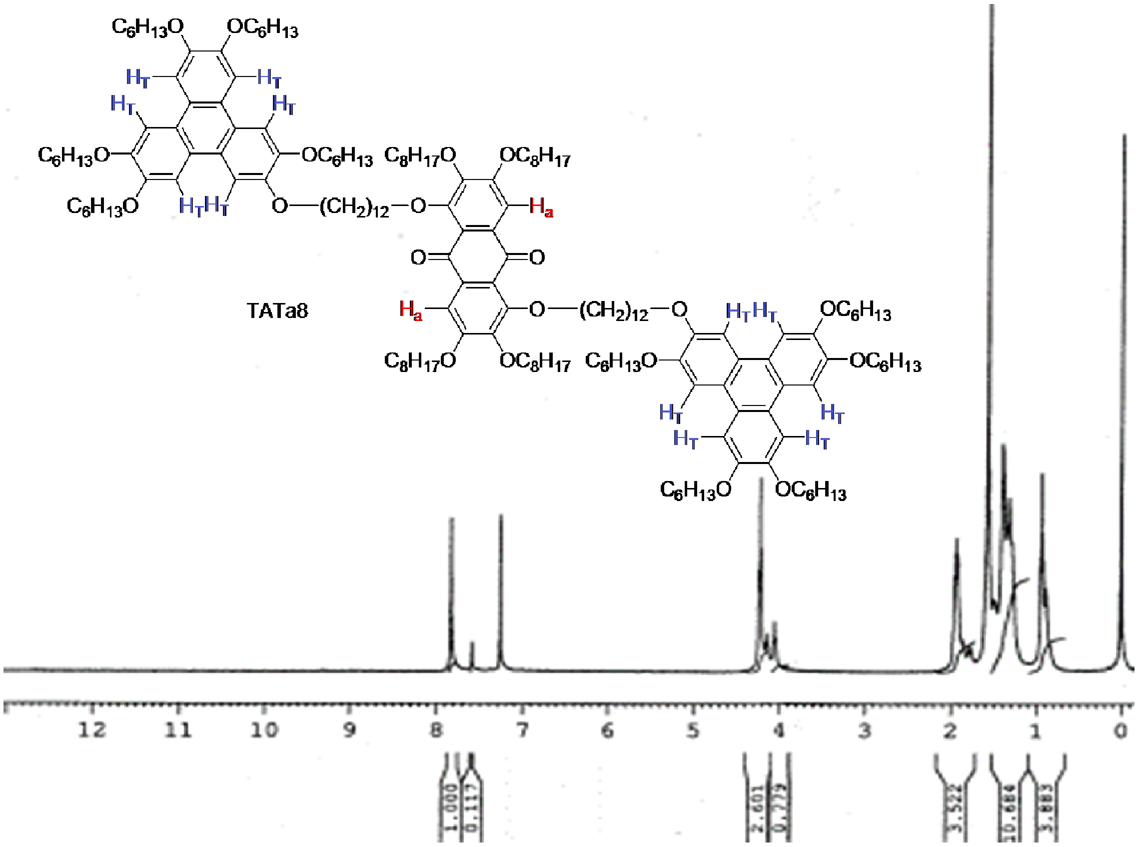


**Figure 3**. $^1$H NMR spectrum of the compound **TATa8**.

Figures 1 and 2 show the $^1$H NMR spectrum of precursors **19** and **23**, respectively. We can compare the NMR spectra of these two precursors with that of **TATa8** (Figure 3). Absence of any peak at δ 12.78 ppm in the spectrum of **TATa8**, which is present in the same of **19** (Figure 1), indicates the complete etherification of two anthraquinone hydroxyl group. Similarily, the triplet peak related to –$CH_2Br$ protons (Figure 2) of **23** is also abscent in the spectrum of **TATa8**. There are two different types of aromatic protons which give rise to two signals at different δ values. As seen from the structure above, protons $H_a$ and $H_a$ which are attached to 4- and 8- positions of anthraquinone nucleus are in the same environment and appear as a singlet at δ = 7.59. Twelve aromatic protons $H_T$ of triphenylene moiety appear at δ 7.83 ppm. The –$OCH_2$ protons of peripheral alkyl chains of triphenylene, anthraquinone and ethereal methylene spacer connecting the two rings can be clearly seen in the spectrum at δ

4.0-4.3 ppm. The end methyl protons can be observed at δ 0.93 ppm. Other aliphatic protons of the peripheral alkyl chains and spacers can be visibly perceived in the spectrum at δ 1.2-2.0 ppm. This confirms the structure and high purity of the compound. All other derivatives **TATa6-14**, **TATb6-14**, show similar spectrum differing only in the the number of aliphatic protons.

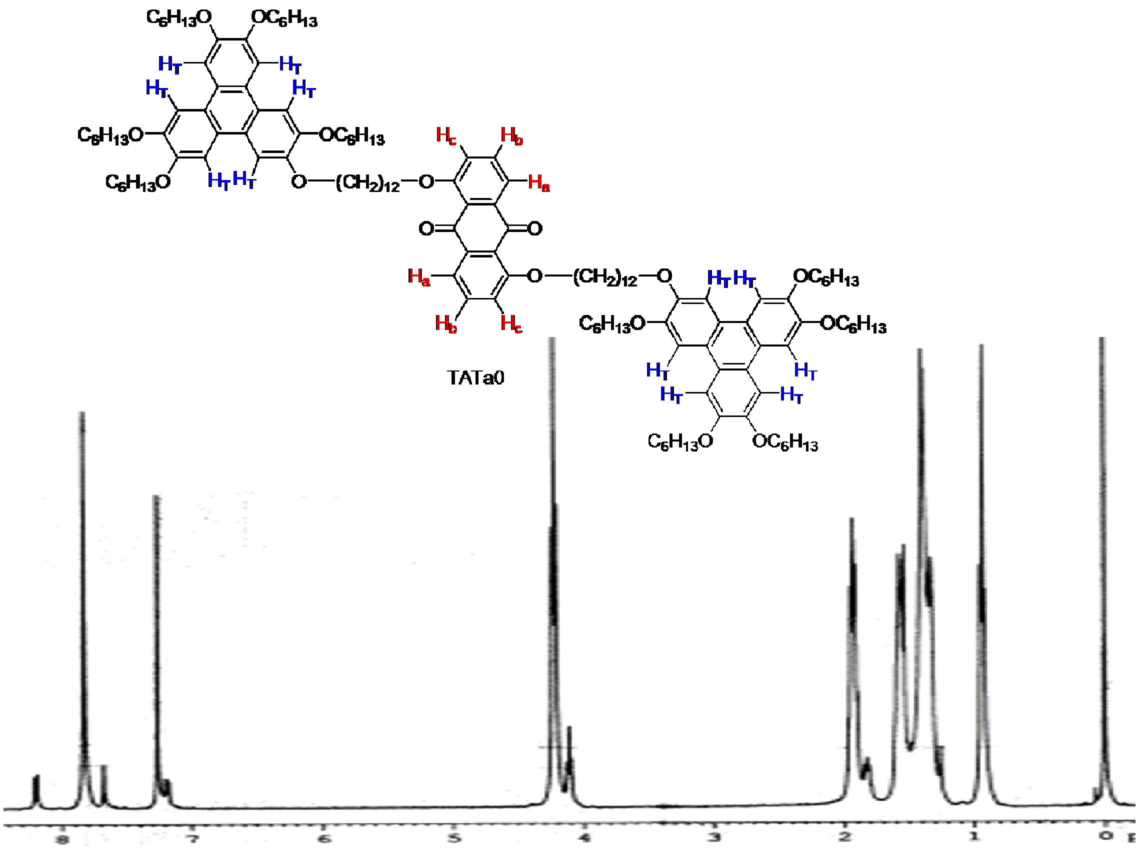


**Figure 4**. $^1$H NMR spectrum of the compound **TATa0**.

Figure 4 represents the $^1$H NMR spectrum of **TATa0**. There are four different types of aromatic protons which give rise to four signals at different δ values. As compared to **TATa8**, NMR of this trimer shows two additional peaks in aromatic region corresponding to anthraquinone aromatic protons $H_b$ and $H_c$. These protons appear as double doublet (coupled with $H_a$ and $H_c$) and doublet (coupled with $H_b$) with δ values 7.2 and 8.19 ppm, respectively.

While proton $H_a$ resonates as a doublet (coupled with $H_b$) at 7.67 pm, all the other protons appears in a similar way to those of trimer **TATa8**.

## 4.8.2. Thermal behavior of donor-acceptor-donor triads

The thermal behavior of all the compounds was investigated by polarizing optical microscopy (POM) and differential scanning calorimetry (DSC). In the case of materials which were mesomorphic, classical textures of discotic columnar mesophases appeared upon cooling from the isotropic liquid as shown in Figure 5.

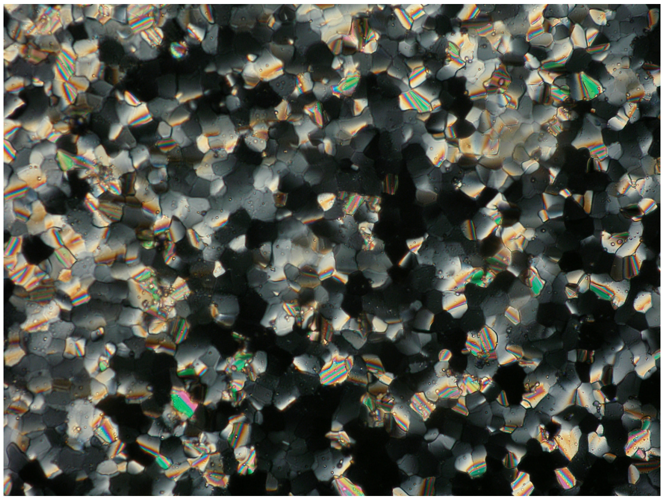


**Figure 5.** Optical micrograph of **TATa6** at 80 °C on cooling from the isotropic liquid (crossed polarizer, magnification × 200).

These textures are similar to the known textures for $Col_h$ phases. All the trimers contain two identical triphenylenes substituted with five hexyloxy peripheral chains linked to the central anthraquinone moiety through 12 (**TATa** series) or 10 (**TATb** series) methylene spacer. In both the series the peripheral alkyl chain lengths around the anthraquinone core varies from hexyloxy to tetradecyloxy. The transition temperature and associated enthalpy data obtained from the heating and cooling cycles of DSC are collected in Table 1. The peak temperatures are given in $^{o}$C and the numbers in parentheses indicate the transition enthalpy ($\Delta H$) in kJ/mol.

**Table 1.** Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ/mol. in parentheses) of novel symmetrical trimers.

| Compound* | First Heating scan | First Cooling scan |
|---|---|---|
| **TATa6** | ss 59.1 (3.94) $Col_h$ 104.1(14.8) I | I 99.3 (15.8) $Col_h$ |
| **TATa7** | ss 37 (4.8) g' 67.4 (3.8) $Col_h$ 89.6 (6.0) I | I 81.4 (6.0) $Col_h$ 6.4 (2.3) ss |
| **TATa8** | ss 47.3 (22.2) $Col_h$ 83.0 (6.4) I | I 72.1 (8.0) $Col_h$ |
| **TATa10** | ss 51.2 (23.1) $Col_h$ 59.1 (2.4) I | I 53 (7.0) $Col_h$ 32.6 (2.4) ss |
| **TATa10'** | ss 45.6 (28.5) $Col_h$ 69 (6.2) I | I 57 (7.0) $Col_h$ |
| **TATa14** | Cr 47 (99.5) I | I 18.4 (66.9) Cr |
| **TATb6** | ss 41.5 (23.1) $Col_h$ 69.3 (2.9) I | I 59.7 (3.4) $Col_h$ |
| **TATb7** | ss 45 (50.3) $Col_h$ 65.8 (6.4) I | I 58.6 (6.9) $Col_h$ |
| **TATb10** | Cr 47.5 (6.3) Cr' 63.4 (81.9) I | I 31.4 (2.6) Cr' 21.4(1.1) Cr |
| **TATb10'** | Cr 70.7 (96.1) I | I 45.4 (18.2) $Col_h$ |
| **TATb12** | Cr 44.4 (49.7) I | I 8.6 (30.7) Cr |
| **TATb14** | Cr 60.1 (94.4) I | I 29.7 (81.0) Cr |

* See Scheme 2 for chemical structures. ss: semi solid; Cr: crystal; $Col_h$: hexagonal columnar phase; I: isotropic phase.

The compound **TATa0,** without any peripheral alkyl chains (OR = H) around the central core of the trimer, does not exhibit any liquid crystalline property. It melts from crystalline solid state to isotropic liquid state at 39.7 $^{o}$C on heating and on cooling it crystallizes slowly over a period of time at room temperature. This could be because the absence of alkyl chains around the core does not provide the space filling effect of alkyl chains which is crucial for exhibiting mesophase behavior in discotic liquid crystals. The highest homologue of the series **TATa14** also does not display any liquid crystalline property, it passes from crystalline solid state to isotropic liquid state at 47 °C on heating and on cooling the isotropic liquid crystallizes at 18.4 °C. This could be because the longer alkyl chains around the central anthraquinone core may hinder the self-assembly of molecules. All other members of the **TATa** series **TATa6**, **TATa7**, **TATa8**, **TATa10** and **TATa10’** display enantiotropic mesophase behavior. In their DSC thermograms, they display a soft solid to mesophase transition followed by mesophase to isotropic transition on heating. Upon cooling they show only isotropic to mesophase transition and the mesophase remains stable down to room temperature or partially solidified at low temperature. As a typical example the DSC thermogram of compound **TATa6** is shown in Figure 6. On increasing the alkyl chain length around the anthraquinone core the mesophase to isotropic transition temperatures of the trimers decrease as shown in the Figure 7. This could be because the longer alkyl chains introduce more intracolumnar disorder and hence the core-core unstacking becomes easy.

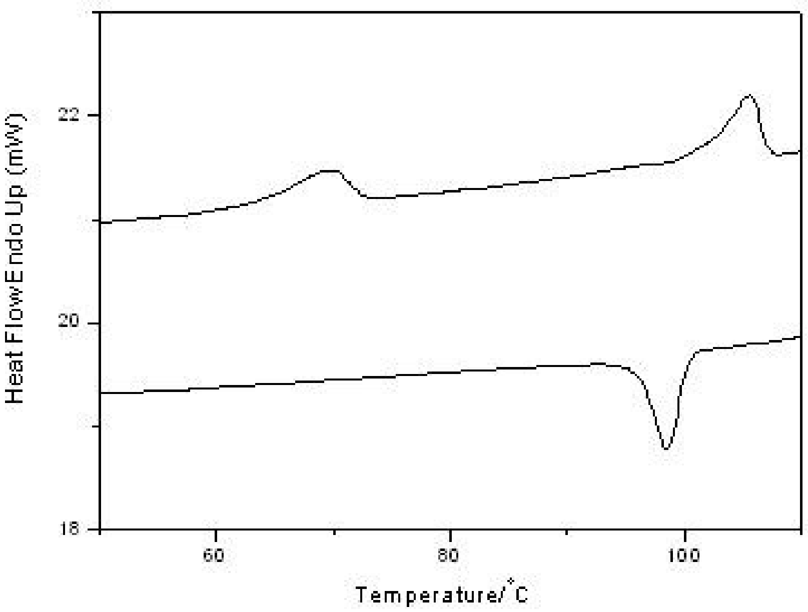


**Figure 6.** DSC thermogram of the trimer **TATa6** on heating and cooling cycles (scan rate 10 °C/min).

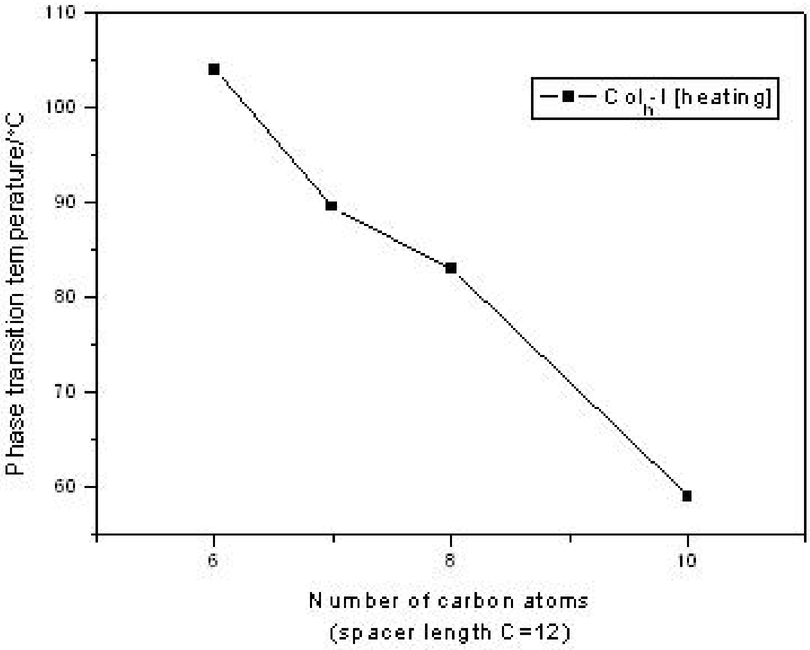


**Figure 7.** Variation of Phase transition temperatures of **TATa6-TATa10** with number of carbon atoms in the peripheral alkyl chains of anthraquinone.

In series **TATb** only two trimers **TATb6** and **TATb7** were found to display enantiotropic liquid crystalline property. Compound **TATb10'** shows monotropic phase behavior. Other trimers **TATb10**, **TATb12** and **TATb14** of the series do not exhibit any liquid crystalline property. They show only crystalline to isotropic and isotropic to crystalline transitions on heating and cooling, respectively. This is not surprising as the spacer connecting the donor with the acceptor is short, long peripheral substitution around the central core can disturb their packing. The absence of mesophase in compound **TATa14**, **TATb10**, **TATb12** and **TATb14** clearly indicates that when the peripheral chain lengths of the central core are either equal to or longer than the spacer length then these symmetrical trimers do not exhibit any liquid crystalline property. Shorter alkyl chains around the central core stabilize the mesophase in these discotic trimers. If we compare the mesophase stability between compound **TATa10** and **TATa10'** having the same mass unit around the central core, the compound **TATa10'** shows wider mesophase range of 23.4 °C compared to 7.9 °C of compound **TATa10**. Similarly on comparing **TATb10** and **TATb10**' we find that compound **TATb10** does not exhibit any liquid crystalline property but compound **TATb10**' displays a monotropic phase behavior. The above trimers contain same mass units around the central core but the alkyl chain lengths around the central core are different. Both **TATa10’** and **TATb10’** contain shorter chain lengths *i.e.* 3, 7-dimethyloctyl as compared to **TATa10** and **TATb10** with longer decyl chains.

## 4.8.3. X-ray diffraction studies

In order to reveal the mesophase structure and hence the supramolecular organization of these compounds, X-ray diffraction experiments were carried out using unoriented samples. X-ray diffraction patterns for all the trimers were recorded in the columnar phase 10 °C below the clearing temperature while cooling from the isotropic phase. The X-ray diffraction patterns of the mesophase exhibited by all the samples belonging to both the series is supportive of a discotic hexagonal columnar arrangement. As a typical example, the X-ray diffraction pattern of compound **TATa6** and its one dimensional intensity *vs* theta ($\theta$) graph derived from the pattern are shown in the Figure 8. Qualitatively all the compounds show similar X-ray diffraction patterns.

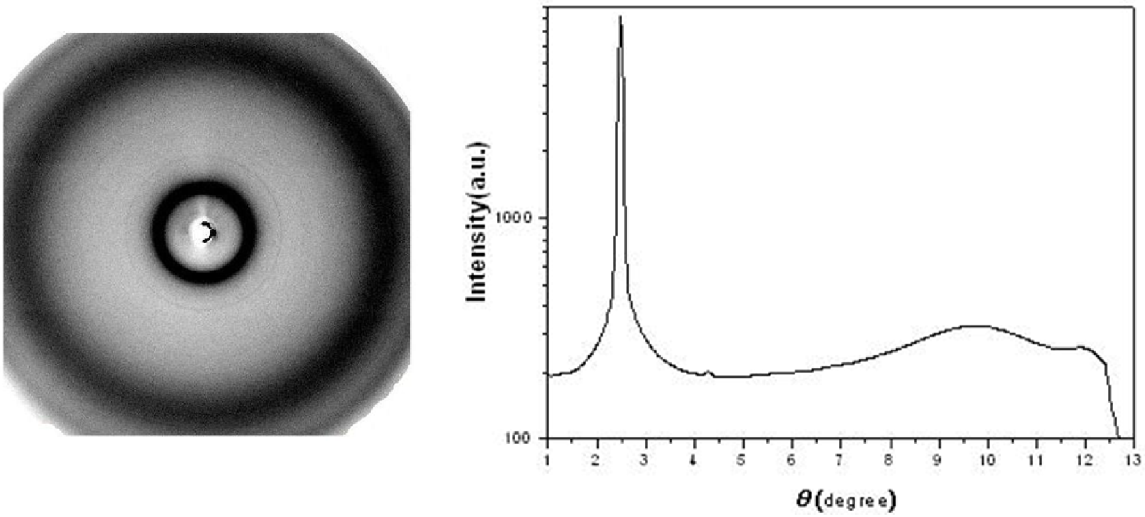


**Figure 8.** X-Ray diffraction pattern of the trimer **TATa6** at 85 °C and its intensity vs $\boldsymbol{\theta}$ profile.

As can be seen from the Figure 8, in the small angle region, two sharp peaks, one very strong and one weak reflection are seen whose *d*-spacings are in the ratio of 1:1/√3, consistent with a two-dimensional hexagonal lattice. In the wide angle region two diffuse reflections are seen. The broad one centered at 4.62 Å corresponds to the liquid like order of the aliphatic chains. The reflection at higher *theta* ($\theta$) value and well separated from the previous one is due to the stacking of the molecular cores one on the top of the other. The diffuse nature of this peak implies that the stacking of the discs within each column is correlated over short distances only. The average stacking distance (core-core separation) was found to be 3.66 Å and falls in the range observed for a number of materials exhibiting discotic columnar phase. So the discotic molecules stack one on top of the other to form the columns and these columns in turn arrange themselves on a two dimensional hexagonal lattice for both the series of compounds. The intercolumnar distances, $a$, calculated using the relation $a = d_{10}/\cos 30^{o}$, where $d_{10}$ is the spacing corresponding to the strong peak in the small angle region, for all the compounds are listed in Table 2.

**Table 2.** Inter and intra columnar distances (Å) of the trimers derived from their diffraction patterns.

| **Compound*** | ***d*-Spacing (Å)** | **Intercolumnar distance (Å)** | **Intracolumnar distance (Å)** |
|---|---|---|---|
| **TATa6** | 17.71 | 20.45 | 3.58 |
| **TATa7** | 17.80 | 20.56 | 3.65 |
| **TATa8** | 18.15 | 20.96 | 3.66 |
| **TATa10** | 18.59 | 21.47 | 3.66 |
| **TATa10'** | 18.13 | 20.93 | 3.73 |
| **TATb6** | 17.33 | 20.01 | 3.66 |
| **TATb7** | 17.43 | 20.13 | 3.65 |
| **H6TP** | 19.5 | 22.52 | 3.56 |
| **H6AQ** | 18.19 | 21.0 | 3.6 |

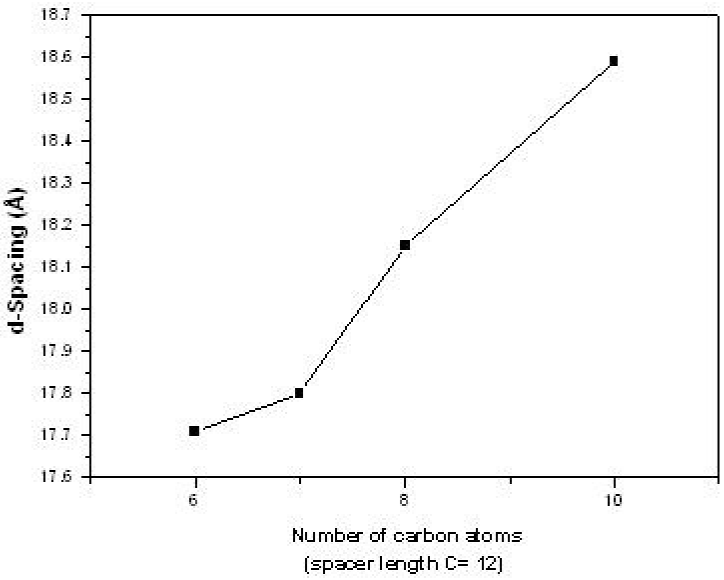


**Figure 9**. Variation of *d*-spacing value with respect to side chain length.

In both the series it is evident that as alkyl chain lengths increase the diameter of the cylindrical columns formed by the discotic molecules also increases as shown in the Figure 9. The intercolumnar distances varies from 20.5-21.5 Å whereas the intracolumnar distance is around 3.7 Å which is usually observed for discotic columnar mesophases. In these unoriented samples, we do not observe any additional small angle peak for the formation of a superlattice arising from the ideal top-on-top stacking of the trimer molecules which could lead to the formation of columnar double cables. Therefore, it was concluded that the triphenylene and anthraquinone subunits arrange themselves statistically to form a columnar hexagonal phase. The intercolumnar distance for hexahexyloxytriphenylene (**H6TP**) and hexahexyloxyanthraquinone (**H6AQ**) is 22.52 Å,[36] and 21.0 Å,[37] respectively but the intercolumnar distance of the symmetrical trimer **TATa6** is 20.45 Å which is less than the corresponding monomers. This minor shrinkage of the intercolumnar distance in the trimer is expected upon covalent linking the two molecules. On comparing the X-ray diffraction results of **TATa6** with **TATb6** and **TATa7** with **TATb7** (Table 2)**,** it is evident that the

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[36] E. O. Arikainen, N. Boden, R. J. Bushby, J. Clements, B. Movaghar, A. Wood,*J. Mater. Chem.* 12, 2161, **1995**.

[37] C. Carfagna, P. Iannelli, A. Roviello, A. Sirigu, *Liq. Cyst.,* 5, 611, **1987**.

intercolumnar distance is decreasing with decreasing spacer length. This is due to shortening of hexagonal lattice with decreasing the length of spacer linking the discotic moieties. As expected, the intercolumnar distance of **TATa10** is more than that of **TATa10’** since **TATa10** contains longer alkyl chains around the central anthraquinone core than **TATa10’** though they contain same mass units around the anthraquinone core. But the intracolumnar distance of **TATa10** is less than **TATa10’**, this is because of the steric effect exerted by the branched alkyl chains around the central core of **TATa10’** which will hinder the discotic cores coming closer in columns.

## 4.8.4. Absorption studies

As the trimers contain electron donor and electron acceptor moieties, it is expected that they may show charge transfer absorption. However, the UV spectrum of the trimer **TATa10** (Figure 10) does not show any additional absorption band as compared to the separate hexaalkoxytriphenylene **(H6TP)** and hexaalkoxyanthraquinone (**RF6C4**). It is essentially a sum of donor and acceptor units.

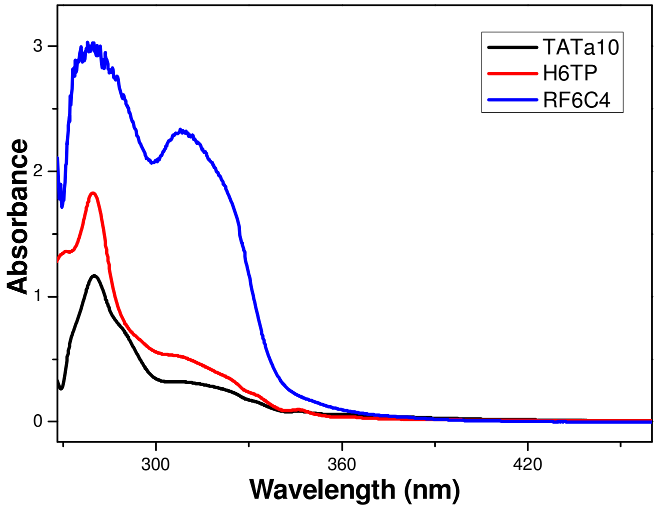

**Figure 10**. Ultraviolet spectra of chloroform solution of **TATa10** and its indivisual monomers (Hexaalkoxy anthraquinone **RF6C4** and Hexaalkoxytriphenylene **H6TP**).

The colour of the trimer **TATa10** is almost matching with the colour of the acceptor. This implies that there is no or very week charge transfer interaction between donor and acceptor units. Similar behavior has previously been reported for other non-liquid crystalline as well as liquid crystalline donor-acceptor dimers.[22-24]

## 4.8.5. Electrical conductivity study

The DC conductivity of pure trimer **TATa7** was performed in indium tin oxide (ITO) coated glass sandwich cells (7 mm × 8 mm) with a separation of 5.96 µm. The current measurements were carried out using a Keithley pico ammeter (Model 480) along with a constant voltage source and a temperature controller. The samples were introduced into a glass capillary by heating to isotropic stage and the cooled to room temperature along with two gold coated copper wires at two ends which gets sealed during cooling. Figure 11 shows the DC conductivity values measured at different temperatures for pure trimer **TATa7**, while cooling from isotropic temperature.

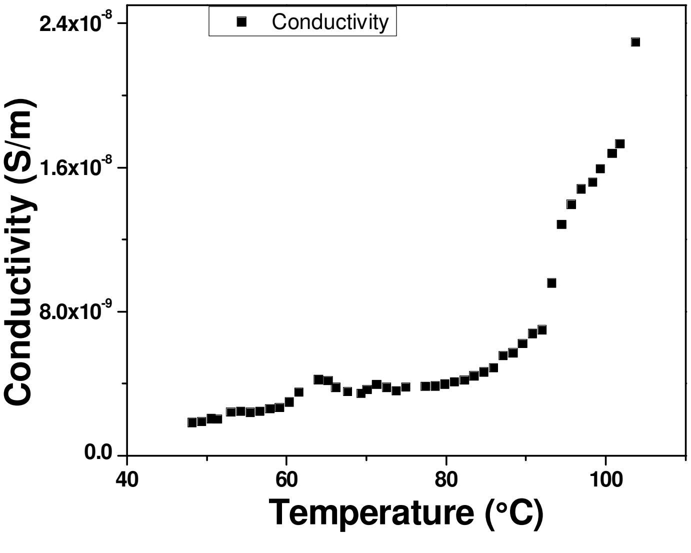

**Figure 11**. Variation of measured dc conductivity values as a function of temperature for **TATa7**.

The conductivity was measured as a function of temperature while cooling scan from 103.7 °C to 48.2 °C. The measured conductivity decreases on decreasing temperature. A change in the slope of the conductivity-temperature plot is observed at 94.5 °C. The conductivity is decreasing gradually between 92 °C (7 x $10^{-9}$ S/m) and 73.8 °C (3.6 x $10^{-9}$ S/m) At lower temperature (below 73.8 °C), there is too much fluctuation in the conductivity value. The highest and lowest values of measured conductivity in the liquid crystalline range are 4.1 x $10^{-9}$ S/m (at 81.1 °C) and 1.8 x $10^{-9}$ S/m (at 48.2 °C), respectively. These conductivity values are slightly greater as compared to the same measured in case of pure hexaheptyloxytriphenylene in its liquid crystalline range.[38] However dc conductivity of this trimer is about two orders of magnitude greater than the same obtained in case of hexa(hexylthio)triphenylene.[39] It is notable that the variation in conductivity with respect to tempetarure does not match with transition temperatures observed while cooling in DSC (Table 1, Figure 11). This can be explained in terms of orientation behavior of discs within the column. Phase transition is a thermodynamic phenomenon, directly related to enthalpy associated with the phase transition. Conductivity, on the other hand is bluntly associated with the degree of orientation of triphenylene or anthraquinone rings within the column. Secondly, discotic oligomers are very much sensitive to heating and cooling rates. In the present case the cooling rate throughout the measurement of conductivity was adjusted to 1.5 °C $min^{-1}$, which is very low as compared to the scan rate of 10 °C $min^{-1}$ in DSC measurement.

## 4.9. Conclusion

In conclusion, we have synthesized two series of novel symmetrical liquid crystalline trimers based on anthraquinone and triphenylene moieties using microwave irradiation. The etherification of H-bonded hydroxyl groups of tetraalkoxy anthraquinone with bulky ω-bromo-substituted triphenylenes failed to produce the desired triads under classical reaction conditions. Mesophase behavior of the symmetrical trimers was studied by polarizing optical microscopy and differential scanning calorimetry. They exhibit columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these donor-

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[38] S. Kumar, S. K. Pal, K. P. Suresh, V. Lakshminarayanan, *Soft Matter*, 3, 896, **2007**.

[39] G. B. M. Vaughan, P. A. Heiney, J. P. McCauley Jr, A. B. Smith III, *Phys. Rev b*, 46, 5, 2787, **1992**.

acceptor-donor triads was established by X-ray diffraction studies. Longer spacer length, smaller peripheral alkyl chain length and branching in peripheral alkyl chain of anthraquinone are in favor of liquid crystalline property in these symmetrical trimers.

## 4.10. Experimental

### 4.10.1. General information

General experimental conditions have been described in chapter 2.

### 4.10.2. Synthesis

#### 4.10.2.1. Synthesis of 1,2,3,5,6,7-hexahydroxyanthraquinone (16) (rufigallol)

Rufigallol is prepared following the reported procedure.[5] A mixture of gallic acid **15** (10 g) and conc. $H_2SO_4$ (40 ml) was heated with stirring at 100 ºC for 3h. The reaction mixture was cooled and poured over crushed ice and the orange precipitate obtained was filtered and washed with cold water, dried under high vacuum to get crude rufigallol as a brown solid (4 g, 49 %). The crude rufigallol was used in the subsequent steps without any further purification.

#### 4.10.2.2. Synthesis of 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone (19): General procedure.

In a typical reaction, to a stirred solution of NaOH (4 eq.) in dry DMSO (50 ml) added crude rufigallol **16** (5 g, 0.164 mmol, 1 eq) and 1-bromoalkane (4.4 eq.), and the mixture was heated to 70 ºC and held at the same temperature under $N_2$ for 18h. The reaction mixture was cooled, diluted with aq. HCl and extracted with chloroform (80 ml X 5). The combined chloroform extracts were washed with water and dried over anhydrous $Na_2SO_4$. Product was crystallized from EtOH: $CHCl_3$ (4:6). Yield 45 % (yellow solid).

**$^1$H NMR** (400 MHz, $CDCl_3$): All the compounds give similar spectra differing in only the number of alkyl chain $CH_2$ protons. δ 12.8 (s, 2H), 7.4 (s, 2H), 4.1 (t, 6.5, 8H), 1.9-1.7 (m, alkyl chain $CH_2$), 1.0 (t, 12H).

### 4.10.2.3. Preparation of ω-bromo-substituted triphenylene (23): General Procedure.

In a typical reaction, a mixture of monohydroxy pentahexyloxy triphenylene (1 g), 1, 12-dibromoalkane (2.62 g, 6 eq) and anhydrous potassium carbonate (742 mg, 4 eq) in methyl ethyl ketone was heated to reflux for overnight. The solvent was evaporated in rotatory evaporator. The dried crude material was purified by column chromatography over silica gel (eluant: 3% ethyl acetate in hexane) to afford the desired product.

### 4.10.2.4. Synthesis of donor-acceptor-donor triads (TATa10): General Procedure.

In a typical reaction, A mixture of compound **23** (n = 12) (300 mg, 0.30 mmol), **19** (R = $C_{10}H_{21}$) (43 mg**,** 0.05 mmol) and $Cs_2CO_3$ (200 mg, 0.61 mmol) in NMP (0.5 mL) was irradiated in microwave oven for 30 seconds. The vial was removed from the oven and left to stand for about 1 minute and again irradiated for 30s. This process was repeated for 20 times till the reaction completes (TLC monitoring). The cooled reaction mixture was then poured into excess of distilled water and extracted with chloroform. The organic extract was dried over anhydrous sodium sulphate, concentrated and the product was purified by repeated column chromatography over silica gel (eluant: 4% ethyl acetate in hexane). Solvent was then removed in rotary evaporator. The residue left was now dissolved in dichloromethane and the resulting solution was added to cold methanol to afford **TATa10** (34 mg, 25%).

**TATa10**

**$^1$H NMR:** (400MHz, $CDCl_3$): δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.06 (t, *J* = 6.2 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.5 Hz, 4H), 0.8-1.6 (m, 190H). **$^{13}$C NMR:** (100 MHz, $CDCl_3$): δ 181.2, 157.5, 153.9, 149.1, 147, 132.7, 123.7, 107.6, 107.1, 77.3, 77, 76.7, 75.9, 74.7, 74.1, 69.8, 69.2, 31.9, 31.7, 30.4, 29.5, 29.4, 26.1, 25.9, 22.7, 21.3, 18.5, 15.9, 14.0.

**Elemental analysis:** Calcd for $C_{174}H_{276}O_{20}$, C 77.75, H 10.35; Found C 77.32, H 10.53%.

## Data for other compounds

**TATa6:**

**$^1$H NMR:** δ 7.83 (s, 12H ), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.5 Hz, 4H), 0.8-1.6 (m, 158H).

**Elemental analysis:** Calcd for $C_{158}H_{244}O_{20}$, C 77.03, H 9.98; Found C 76.63, H 9.98%.

**TATa7:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 166H).

**Elemental analysis:** Calcd for $C_{162}H_{252}O_{20}$, C 77.22, H 10.08; Found C 76.91, H 10.04%.

**TATa8:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.5 Hz, 4H), 4.06 (t, *J* = 6.2 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 6.9 Hz, 4H), 0.8-1.6 (m, 174H).

**Elemental analysis:** Calcd for $C_{166}H_{260}O_{20}$, C 77.40, H 10.17; Found C 77.13, H 9.82%.

**TATa10':**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.61 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.5 Hz, 4H), 4.06 (t, *J* = 6.2 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 6.9 Hz, 4H), 0.8-1.6 (m, 190H).

**Elemental analysis:** Calcd for $C_{174}H_{276}O_{20}$, C 77.75, H 10.35; Found C 77.32, H 10.89%.

**TATa14:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.3 Hz, 4H), 4.06 (t, *J* = 5.6 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 222H).

**Elemental analysis:** Calcd for $C_{190}H_{308}O_{20}$, C 78.35, H 10.66; Found C 77.96, H 10.71%.

**TATb6:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.15 (t, *J* = 6.4 Hz, 4H), 4.06 (t, *J* = 6.4 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 150H).

**Elemental analysis:** Calcd for $C_{154}H_{236}O_{20}$, C 76.83, H 9.88; Found C 76.37, H 9.89%.

**TATb7:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.8 Hz, 4H), 4.06 (t, *J* = 6.3 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 7.4 Hz, 4H), 0.8-1.6 (m, 158H).

**Elemental analysis:** Calcd for $C_{158}H_{244}O_{20}$, C 77.03, H 9.98; Found C 76.62, H 10.36%.

**TATb10:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.3 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 182H).

**Elemental analysis:** Calcd for $C_{170}H_{268}O_{20}$, C 77.58, H 10.26; Found C 77.31, H 10.23%.

**TATb10':**

**$^1$H NMR:** δ 7.84 (s, 12H, Ar-H ), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.3 Hz, 4H), 4.06 (t, *J* = 6.5 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 182H).

**Elemental analysis:** Calcd for $C_{170}H_{268}O_{20}$, C 77.58, H 10.26; Found C 77.14, H 10.00%.

**TATb12:**

**$^1$H NMR:** δ 7.84 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.3 Hz, 24H), 4.14 (t, *J* = 6.3 Hz, 4H), 4.06 (t, *J* = 6.2 Hz, 8H), 1.94 (m, 32H), 1.77 (q, *J* = 7.8 Hz, 4H), 0.8-1.6 (m, 190H).

**Elemental analysis:** Calcd for $C_{178}H_{284}O_{20}$, C 77.91, H 10.43; Found C 77.78, H 10.30%.

**TATb14:**

**$^1$H NMR:** δ 7.83 (s, 12H), 7.59 (s, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 4.14 (t, *J* = 6.4 Hz, 4H), 4.06 (t, *J* = 6.3 Hz, 8H), 1.94 (m, 32H), 1.78 (q, *J* = 7.6 Hz, 4H), 0.8-1.6 (m, 198H).

**Elemental analysis:** Calcd for $C_{186}H_{300}O_{20}$, C 78.21, H 10.59; Found C 78.16, H 10.53%.