Microwave-assisted facile synthesis of discotic liquid crystalline symmetrical donor–acceptor–donor triads

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We report the synthesis and characterization of two series of novel triphenylene–anthraquinone-based symmetric discotic liquid crystalline trimers. These triads were prepared using microwave dielectric heating. Conventional heating under similar reaction conditions failed to produce desired products. To the best of our knowledge, these are the first donor–acceptor–donor triads in which all the three components represent discotic mesogenic moieties. Chemical structures of these discotic oligomers have been characterized by spectral techniques and elemental analysis. The thermotropic liquid crystalline properties of these donor–acceptor–donor triads were investigated by polarizing optical microscopy and differential scanning calorimetry. They exhibit a columnar mesophase over a wide range of temperature. The columnar hexagonal mesophase structure of these discotic oligomers has been elucidated with the help of X-ray diffraction studies.

Introduction

The notable improvement in the performance of electronic devices based on organic semiconductors has attracted great interest in recent years.[1] The improved efficiency of organic devices has origins ranging from appropriate molecular design to well-defined structured layers essential for effective charge transport. 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 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 self-assembly will be crucial for the development of nano-engineered functional materials for electronic applications.[1] Among the diverse semiconductors, discotic liquid crystals (DLCs) play an important role in the design of electronic devices.[2] Discotic liquid crystals are unique nanostructures with remarkable electronic and optoelectronic properties. Due to the co-facial stacking of aromatic cores, disc-like molecules self organize into one dimensional columnar wire and these columns in turn arrange themselves in various two-dimensional lattices. The transport along the columnar axis is much faster than between the columns. Due to their relatively high charge carrier mobility, tendency to form highly order films of various thickness and self healing of defects owing to their dynamic nature, discotic mesogens have been considered as attractive candidates for applications in organic electronic devices such as photovoltaic solar cells, light emitting diodes and field effect transistors.[2]

Microwave-assisted high-speed chemical synthesis has attracted a considerable amount of attention in the past decade. Almost all types of organic reactions have been performed using the efficiency of microwave-flash heating. This is not only due to the fact that reactions proceed significantly faster and more selectively than under conventional thermal conditions but also because of the operational simplicity, high yield of products and cleaner reactions with easier work-up. A large number of review articles provide extensive coverage of the subject.[3] Recently we and others have reported the synthesis of a variety of liquid crystalline materials using microwave dielectric heating.[4]

Very recently a great deal of attention is being paid to liquid crystal oligomers.[5] The physical properties of liquid crystalline oligomers are significantly different from those of conventional low molar mass liquid crystals. Their purification and characterization are simple, and due to the restricted motion of their components liquid crystal oligomers provide and stabilize a variety of fluid phases with fascinating functions. Further, an oligomeric approach provides a wide flexibility in molecular design towards multifunctional liquid crystals. However, compared to the number of calamitic oligomers, discotic oligomers are rare. In this context we are interested in the design and synthesis of novel functional discotic oligomeric materials and their mesophase behavior. Our molecular design is such that it contains the well studied electron rich triphenylene moiety[6] and electron deficient anthraquinone[7] as the hole and electron transporting components, respectively. 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,[8] 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

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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.

Experimental

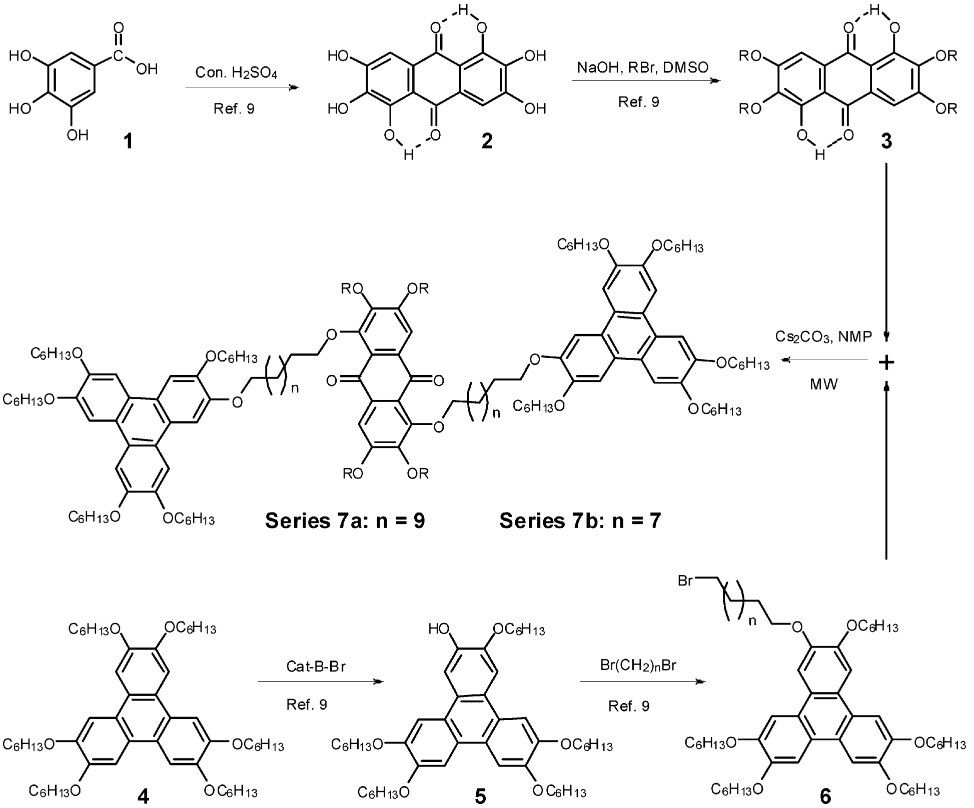
General information

Chemicals and solvents (AR quality) were used as received without any further purification. Microwave irradiation was performed in an unmodified household microwave oven. (LG, MS-192W). However, commercial microwave reactors for organic reactions are now available which provides adequate mixing and control of reaction parameters such as temperature and pressure. Column chromatographic separations were performed on silica gel (230–400 mesh). Thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60, F254). Chemical structure characterization of the compounds was carried out through a combination of ^{1}H NMR, ^{13}C NMR (Bruker AMX 400 spectrometer) and elemental analysis (Carlo-Erba EA1112 analyzer). ^{1}H NMR spectra were recorded using deuterated chloroform ($CDCl_3$) as solvent. Tetramethylsilane (TMS) was used as an internal standard. The transition temperatures and associated enthalpy values were determined using a differential scanning calorimeter (DSC; Perkin-Elmer, Model Pyris 1D) which was operated at a scanning rate of 5 °C min^{-1} both on heating and cooling cycles. The apparatus was calibrated using indium (156.6 °C) as a standard. The textural observations of the mesophase were carried out using polarizing light microscopy (Olympus BX51) provided with a heating stage (Mettler FP82HT) and a central processor (Mettler FP90). X-Ray diffraction studies (XRD) were carried out on unoriented samples using Cu-Kα (λ = 1.54 Å) radiation from a Rigaku Ultrax 18 rotating anode generator (5.4 kW) monochromated with a graphite crystal. The samples were held in sealed Lindemann capillary tubes (0.7 mm diameter) and the diffraction patterns were collected on a two-dimensional Marresearch image plate.

Synthesis of trimers

Rufigallol **2**, 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **3**, hexaalkoxytriphenylene **4**, monohydroxypentaalkoxytriphenylene **5** and ω-bromo-substituted triphenylene **6** were prepared as reported by us previously.[9] All the trimers were prepared following same method which involves alkylation of 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **3** with terminal bromo-substituted triphenylene **6** using microwave dielectric heating. A typical procedure for the synthesis of a representative example **7a10** is given below. The suffix number in the series **7a** and **7b**, represents the number of carbon atoms in the peripheral chains attached with central anthraquinone moiety (R in the structure **7**, Scheme 1).

A mixture of compound **6a** (n = 9) (300 mg, 0.30 mmol), **3** (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 a microwave oven for 30 s. The vial was removed from the oven and left to stand for about 1 min and again irradiated for 30 s. This process was repeated for 20 times until the reaction was complete (TLC monitoring). The cooled reaction mixture was then poured into an excess of distilled water and extracted with chloroform. The organic extract was dried over anhydrous sodium sulfate, concentrated and the product was purified by repeated column chromatography over silica gel (eluent: 4% ethyl acetate in hexane). Solvent was then removed in rotary evaporator. The residue was then dissolved in dichloromethane and the resulting solution was added to cold methanol to afford **7a10** (34 mg, 25%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.4 Hz, 4 H), 4.06 (t, J = 6.2 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.5 Hz, 4 H), 0.8–1.6 (m, 190 H). ^{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: Calc. for $C_{174}H_{276}O_{20}$, C 77.75, H 10.35. Found: C 77.32, H 10.53%. All other compounds give satisfactory spectral and elemental analysis data in accordance with their chemical structure. Selected data for compound **7a6**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.4 Hz, 4 H), 4.06 (t, J = 6.5 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.5 Hz, 4 H), 0.8–1.6 (m, 158 H). Elemental analysis: Calc. for $C_{158}H_{244}O_{20}$, C 77.03, H 9.98. Found: C 76.63, H 9.98%. **7a7**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.4 Hz, 4 H), 4.06 (t, J = 6.5 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 166 H). Elemental analysis: Calc. for $C_{162}H_{252}O_{20}$, C 77.22, H 10.08; Found C 76.91, H 10.04%. **7a8**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.5 Hz, 4 H), 4.06 (t, J = 6.2 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 6.9 Hz, 4 H), 0.8–1.6 (m, 174 H). Elemental analysis: Calc. for $C_{166}H_{260}O_{20}$, C 77.40, H 10.17. Found: C 77.13, H 9.82%. **7a10′**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.61 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.5 Hz, 4 H), 4.06 (t, J = 6.2 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 6.9 Hz, 4 H), 0.8–1.6 (m, 190 H). Elemental analysis: Calc. for $C_{174}H_{276}O_{20}$, C 77.75, H 10.35. Found: C 77.32, H 10.89%. **7a14**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.3 Hz, 4 H), 4.06 (t, J = 5.6 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 222 H). Elemental analysis: Calc. for $C_{190}H_{308}O_{20}$, C 78.35, H 10.66. Found: C 77.96, H 10.71%. **7b6**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.15 (t, J = 6.4 Hz, 4 H), 4.06 (t, J = 6.4 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 150 H). Elemental analysis: Calc. for $C_{154}H_{236}O_{20}$, C 76.83, H 9.88. Found: C 76.37, H 9.89%. **7b7**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.8 Hz, 4 H), 4.06 (t, J = 6.3 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 7.4 Hz, 4 H), 0.8–1.6 (m, 158 H). Elemental analysis: Calc. for $C_{158}H_{244}O_{20}$, C 77.03, H 9.98. Found: C 76.62, H 10.36%. **7b10**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.3 Hz, 4 H), 4.06 (t, J = 6.5 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 182 H). Elemental analysis: Calc. for $C_{170}H_{268}O_{20}$, C 77.58, H 10.26. Found: C 77.31, H 10.23%. **7b10′**: ^{1}H NMR: δ 7.84 (s, 12H, Ar–H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.3 Hz, 4 H), 4.06 (t, J = 6.5 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 182 H). Elemental analysis: Calc. for $C_{170}H_{268}O_{20}$, C 77.58,



Scheme 1 Synthetic route of triphenylene–anthraquinone trimers. **7a** Series: OR = H (**7a0**); R = *n*-C_6H_{13} (**7a6**); R = *n*-C_7H_{15} (**7a7**); R = *n*-C_8H_{17} (**7a8**); R = *n*-$C_{10}H_{21}$ (**7a10**); R = 3,7-dimethyloctyl (**7a10′**); R = *n*-$C_{14}H_{29}$ (**7a14**); **7b** Series: R = *n*-C_6H_{13} (**7b6**); R = *n*-C_7H_{15} (**7b7**); R = *n*-$C_{10}H_{21}$ (**7b10**); R = 3,7-dimethyloctyl (**7a10′**); R = *n*-$C_{12}H_{25}$ (**7a12**); R = *n*-$C_{14}H_{29}$ (**7a14**).

H 10.26. Found: C 77.14, H 10.00%. **7b12**: ^{1}H NMR: δ 7.84 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.3 Hz, 24 H), 4.14 (t, J = 6.3 Hz, 4 H), 4.06 (t, J = 6.2 Hz, 8 H), 1.94 (m, 32 H), 1.77 (q, J = 7.8 Hz, 4 H), 0.8–1.6 (m, 190 H). Elemental analysis: Calc. for $C_{178}H_{284}O_{20}$, C 77.91, H 10.43. Found: C 77.78, H 10.30%. **7b14**: ^{1}H NMR: δ 7.83 (s, 12 H), 7.59 (s, 2 H), 4.23 (t, J = 6.5 Hz, 24 H), 4.14 (t, J = 6.4 Hz, 4 H), 4.06 (t, J = 6.3 Hz, 8 H), 1.94 (m, 32 H), 1.78 (q, J = 7.6 Hz, 4 H), 0.8–1.6 (m, 198 H). Elemental analysis: Calc. for $C_{186}H_{300}O_{20}$, C 78.21, H 10.59. Found: C 78.16, H 10.53%.

Results and discussion

Synthesis

The synthesis of the novel symmetrical trimers was achieved as shown in Scheme 1. The unequal reactivity of the six phenolic groups of rufigallol **2**, two of which are less reactive by virtue of being intramolecularly hydrogen bonded to the adjacent quinone carbonyls, was exploited. Etherification of rufigallol **2** under mild conditions produced 1,5-dihydroxy-2,3,6,7-tetraalkoxy-9,10-anthraquinone **3** without alkylating the hydrogen bonded C-1 and C-5 positions. These tetraalkoxy derivatives were further alkylated by ω-bromo-substituted triphenylenes with the help of microwave dielectric heating as shown in the Scheme 1, under mild basic conditions to furnish the symmetrical trimers within 10 min, 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 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 °C for 48 h or heating a mixture of **3** and **6** in DMF and NaOH or K_2CO_3 for 48 h did not furnish any product.

Thermal behavior

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 Fig. 1. 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 a 12- (**7a** series) or a 10- (**7b** 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 °C and the numbers in parentheses indicate the transition enthalpy (ΔH) in J g^{-1}. The compound **7a0**, 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

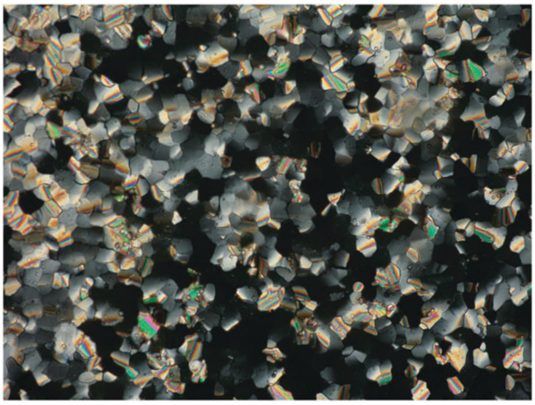


Fig. 1 Optical micrograph of **7a6** at 80 °C on cooling from the isotropic liquid (crossed polarizer, magnification × 200)

39.7 °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 **7a14** 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 **7a** series **7a6**, **7a7**, **7a8**, **7a10** and **7a10′** 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 **7a6** is shown in Fig. 2. On increasing the alkyl chain length around the anthraquinone core the mesophase to isotropic transition temperatures of the trimers decrease as shown in the Fig. 3. This could be because the longer alkyl chains introduce more intracolumnar disorder and hence core–core unstacking becomes easier.

In series **7b** only two trimers **7b6** and **7b7** were found to display enantiotropic liquid crystalline properties. Compound **7b10′** shows monotropic phase behavior. Other trimers **7b10**, **7b12** and **7b14** 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

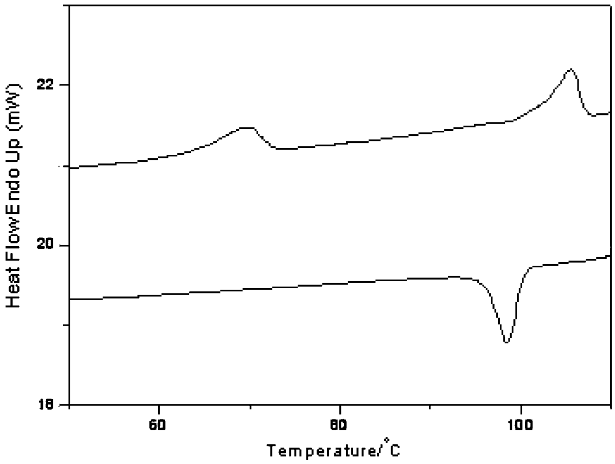


Fig. 2 DSC thermogram of the trimer **7a6** on heating and cooling cycles (scan rate 10 °C min^{-1}).

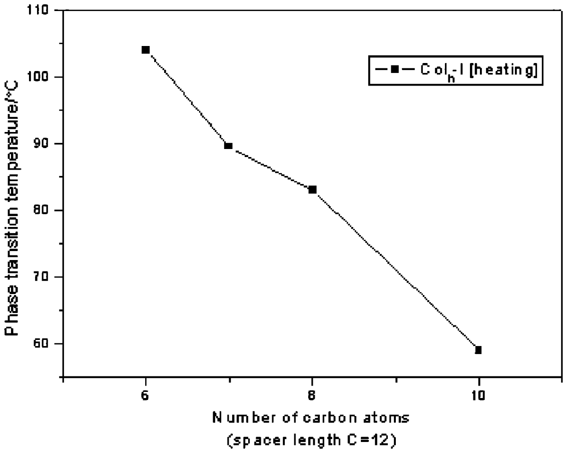


Fig. 3 Variation of phase transition temperatures of **7a6–7a10** with number of carbon atoms in the peripheral alkyl chains of anthraquinone.

Table 1 Phase transition temperatures (peak, °C) and associated enthalpy changes (J g^{-1} in parentheses) of novel symmetrical trimers

Compound[a]	First heating scan	First cooling scan
7a6	ss 59.1 (1.6) Col$_h$ 104.1(6.0) I	I 99.3 (6.4) Col$_h$
7a7	ss 37 (1.9) g′ 67.4 (1.5) Col$_h$ 89.6 (2.4) I	I 81.4 (2.4) Col$_h$ 6.4 (0.9) ss
7a8	ss 47.3 (8.6) Col$_h$ 83.0 (2.5) I	I 72.1 (3.1) Col$_h$
7a10	ss 51.2 (8.6) Col$_h$ 59.1 (0.9) I	I 53 (2.6) Col$_h$ 32.6 (0.9) ss
7a10′	ss 45.6 (10.6) Col$_h$ 69 (2.3) I	I 57 (2.6) Col$_h$
7a14	Cr 47 (34.2) I	I 18.4 (23.0) Cr
7b6	ss 41.5 (9.6) Col$_h$ 69.3 (1.2) I	I 59.7 (1.4) Col$_h$
7b7	ss 45 (20.4) Col$_h$ 65.8 (2.6) I	I 58.6 (2.8) Col$_h$
7b10	Cr 47(2.4) Cr′ 63 (31.1) I	I 31.4 (1.0) Cr′ 21.4(0.4) Cr
7b10′	Cr 70.7 (36.5) I	I 45.4 (6.9) Col$_h$
7b12	Cr 44.4 (18.1) I	I 8.6 (11.2) Cr
7b14	Cr 60.1 (33.1) I	I 29.7 (28.4) Cr

[a] See Scheme 1 for chemical structures. ss: semisolid; Cr: crystal; Col$_h$: hexagonal columnar phase; I: isotropic phase.

the acceptor is short, and so long peripheral substitution around the central core can disturb their packing. The absence of a mesophase in compounds **7a14**, **7b10**, **7b12** and **7b14** 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 **7a10** and **7a10′** having the same mass unit around the central core, the compound **7a10′** shows a wider mesophase range of 23.4 °C compared to 7.9 °C of compound **7a10**. Similarly on comparing **7b10** and **7b10′** we find that compound **7b10** does not exhibit any liquid crystalline property but compound **7b10′** displays a monotropic phase behavior. The above trimers contain the same mass units around the central core but the alkyl chain lengths around the central core are different. Both **7a10′** and **7b10′** contain shorter chain lengths *i.e.* 3,7-dimethyloctyl as compared to **7a10** and **7b10** with longer decyl chains.

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 **7a6** and its one-dimensional intensity *vs.* theta (θ) graph derived from the pattern are shown in the Fig. 4. Qualitatively all the compounds show similar X-ray diffraction patterns. As can be seen from the figure, 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 $1 : 1/\sqrt{3}$, 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 θ 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 a discotic columnar phase. 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 $a = d_{10}/\cos 30°$, 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. 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 Fig. 5. The

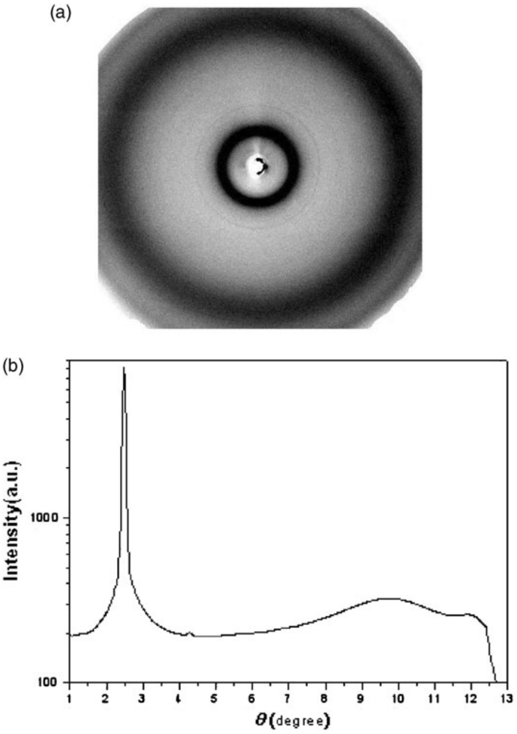


Fig. 4 X-Ray diffraction pattern of the trimer **7a6** at 85 °C and its intensity *vs.* θ profile.

Table 2 Values of *d*-spacings, and of inter- (d_{inter}) and intracolumnar (d_{intra}) distances (Å) of the trimers derived from their diffraction patterns

Compound	*d*-Spacing/Å	d_{inter}/Å	d_{intra}/Å
7a6	17.71	20.45	3.58
7a7	17.80	20.56	3.65
7a8	18.15	20.96	3.66
7a10	18.59	21.47	3.66
7a10′	18.13	20.93	3.73
7b6	17.33	20.01	3.66
7b7	17.43	20.13	3.65
H6TP	19.5	22.52	3.56
H6AQ	18.19	21.0	3.6

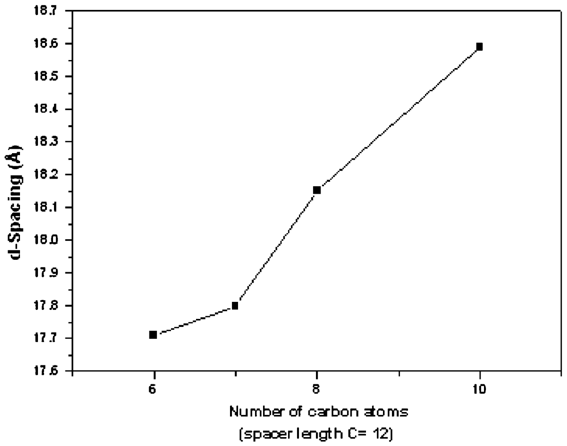


Fig. 5 Variation of *d*-spacing value with respect to side chain length.

intercolumnar distances varies from 20.5–21.5 Å, whereas the intracolumnar distance is constant at 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,[10] and 21.0 Å,[11] respectively, but the intercolumnar distance of the symmetrical trimer **7a6** 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 **7a6** with **7b6** and **7a7** with **7b7** (Table 2), it is evident that the 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 **7a10** is larger than that of **7a10′**, since **7a10** contains longer alkyl chains around the central anthraquinone core than **7a10′**, although they contain the same mass units around the anthraquinone core. However, the intracolumnar distance of **7a10** is less than **7a10′** because of the steric effect exerted by the branched alkyl chains around the central core of **7a10′**, which will hinder the discotic cores coming closer in columns.

Absorption spectra

As the trimers contain both electron donor and acceptor moieties, it is expected that they may show charge transfer absorption. However, the UV-vis spectrum of the trimer **7a10** (Fig. 6) does not show any additional absorption band as compared to the separate hexaalkoxytriphenylene **4** and hexaalkoxyanthraquinone (**RF6C4**) and is essentially a sum of donor and acceptor units. The colour of the trimer **7a10** also almost matches with the colour of the acceptor. This implies that there is no or very weak charge transfer interaction between donor and acceptor units. Similar behaviour has previously been reported for other non-liquid crystalline as well as liquid crystalline donor–acceptor dimers.[9a,12]

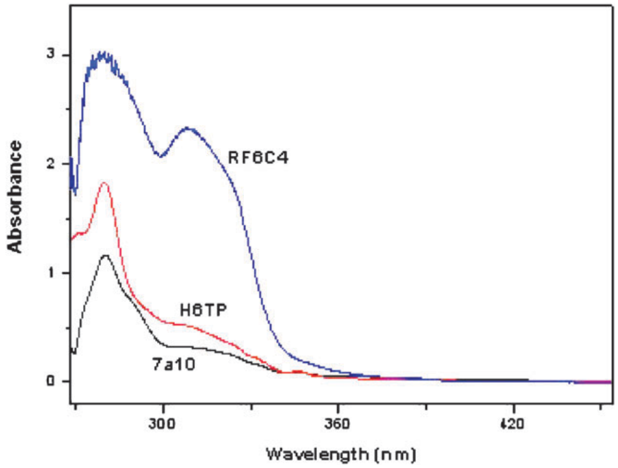


Fig. 6 UV-vis spectra of a chloroform solution of **7a10** and of its individual monomers (hexaalkoxyanthraquinone (**RF6C4**) and hexaalkoxytriphenylene).

Conclusions

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 tetraalkoxyanthraquinones with bulky ω-bromo-substituted triphenylenes failed to produce the desired triads under classical reaction conditions. The mesophase behavior of the symmetrical trimers was studied by polarizing optical microscopy and differential scanning calorimetry and they exhibit a columnar mesophase over a wide range of temperature. Hexagonal columnar structure of the mesophase of these donor–acceptor–donor triads was established by X-ray diffraction studies. Longer spacer length, smaller peripheral alkyl chain length and branching in peripheral alkyl chains of the anthraquinone favor liquid crystalline property in these symmetrical trimers.

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