X = -O- or -COO-

ET13:TNF [1:1]

Intensity(a.u.)

θ

Undoped
TNF:ET13 (1:1) (50% TNF)
TNF:ET13 (2:1) (66% TNF)

Conductivity (S/m)

Temperature (C)

ET13

Intensity(a.u.)

θ

Z range : 1nm

64 nm

64 nm

(a)

Z range : 1 nm

5.5 nm

12 nm

12 nm

(b)

2.1. Liquid crystalline *dimers*

Dimeric liquid crystals or *dimesogens* or *dyads* can be obtained by binding two *identical* or *different* mesogenic units with the help of appropriate spacers. The spacer linking two mesogenic units may be *flexible* (often) or *rigid* (rarely). *Dimers* can be considered as the smallest or simplest possible oligomers and physical properties of liquid crystalline *dimers* are appreciably different to that of conventional low molar mass monomeric liquid crystals because of restricted molecular motions. *Dimers* symbolize ideal model compounds for oligomers or polymers, due to their ease of purification and characterization and the possibility of freezing, in their mesophase, to a glassy state. They often demonstrate thermal behavior, glass transition properties which are characteristic of liquid crystalline polymers. On the other hand these dimesogens retains the fluidity of low molar mass monomesogens. Because of multitalented behavior, these materials are potential candidates for many practical applications.[1]

2.2. History of liquid crystalline *dimers*

Vorlander in 1923 for the first time reported the existence of mesomorphic behavior in mercury-bridged rod shaped *dimers*.[2] He noticed smectic liquid crystalline behavior in diarylmercury Schiff base. Again in 1927,[3] he observed nematic behavior in a dimer in which two rod shaped moieties were connected with the help of methylene spacer. But, it was about more than 50 years after Vorlander's discovery, liquid crystalline *dimers* got a great deal of attention during 1980s. Griffin and Britt, in 1981, reported nematic mesomorphic behavior in

[1] (a) C. T. Imrie, P. A. Henderson, *Chem. Soc. Rev.*, 36, 2096, **2007**; (b) C. T. Imrie, P. A. Henderson, *Current Opinion in Colloid & Interface Science*, 7, 298, **2002**; (c) C. T. Imrie, *Structure and Bonding*, edited by D. M. P. Mingos, Springer-Verlag, Berlin, p. 149, **2001**; (d) C. T. Imrie, G. R. Luckhurst, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H. -W. Spiess, V. Vill, Wiley-VCH, Weinheim, Chap. X, **1998**.
[2] D. Vorlander, *Z. phys. Chem.*, 105, 211, **1923**.
[3] D. Vorlander, *J. Phys. Chem.*, 126, 449, **1927**.

a dimer obtained by coupling two mesogenic units with an aliphatic spacer and coined '*Siamese-twins'* for these type of materials.[4]

2.3.   Classification of liquid crystal *dimers*

2.3.1. Calamitic dimers

Dimers can be categorized into two broad groups: symmetric *dimers* in which the two mesogenic units are *identical* and non-symmetric *dimers* which contain two *different* mesogenic moieties. These two groups can be further sub-divided in accordance with the molecular geometry of the mesogenic moiety.

Figure 1. Sketches of some possible molecular architectures for liquid crystal *dimers*: (a) symmetric calamitic dimer; (b) non-symmetric calamitic dimer; (c) laterally linked symmetric calamitic dimer; (d) laterally linked non-symmetric calamitic dimer.

Some structural possibilities for *dimers* are shown schematically in Figure 1. *Dimers* in which two *identical* mesogens are connected via a *flexible* spacer (Figure 1a) are the most widely synthesized and studied mesogens. However, there are now several examples known in which two *non-symmetric* mesogens are connected (Figure 1b). Figure 1c and 1d represent laterally linked symmetrical and unsymmetrical calamitic *dimers*.

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4 A. C. Griffin, T. R. Britt, *J. Am. Chem. Soc.*, 103, 4957, **1981**.

In addition to these possibilities, several other combinations such as, banana-rod, banana-disk and metal-bridged *dimers* (metallomesogens) and cyclic *dimers* in which two mesogenic units connected to each other via more than one spacer are also possible. These structures have not been shown in Figure 1. Further, all the above-mentioned structures are also possible with a *rigid* spacer instead of a *flexible* spacer. Metal-bridged liquid crystalline *dimers* have also been realized.

2.3.2. Discotic *dimers*

Compared to large number of calamitic *dimers*, the number of reported discotic *dimers* is very less. Similar to calamitic systems, symmetric and non-symmetric discotic *dimers* are also possible.
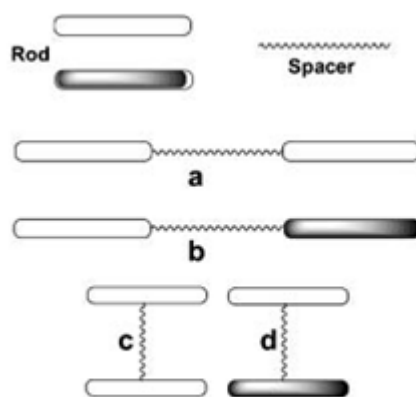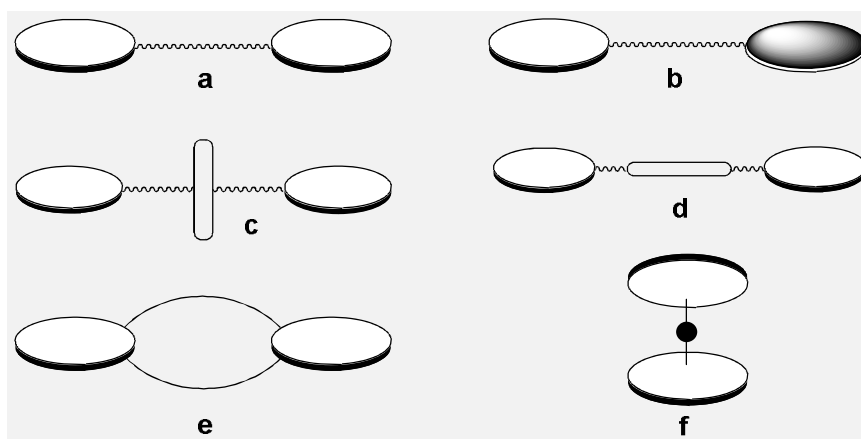

Figure 2. Sketches of some possible molecular architectures for discotic liquid crystal *dimers*: (a) symmetric discotic dimer; (b) non-symmetric discotic dimer; (c) two discogens laterally linked to a calamitic molecule; (d) two discogens terminally linked to a calamitic molecule; (e) cyclic *dimers* in which two mesogenic units are connected to each other via more than one spacer; (f) double decker *dimers* in which two discotic mesogens are tethered via a metal or other atom.

The various structural possibilities for discotic *dimers* are shown schematically in Figure 2. *Dimers* in which two identical discotic mesogens are connected via a flexible spacer (Figure 2a) are the most widely synthesized and studied discotic *dimers*. A few examples of symmetric discotic *dimers* with a rigid spacer instead of a flexible spacer are also known. It is generally difficult to link two different discotic mesogens and, therefore, only a few examples

of unsymmetrical *dimers* (Figure 2b) are realized. *Dimers* in which two discogens connected laterally or linearly to a calamitic molecule are depicted in Figure 2c and 2d, respectively. Cyclic *dimers* (Figure 2e) in which two mesogenic units connected to each other via more than one spacer are also known. A number of double decker *dimers* (Figure 2f) in which two discotic mesogens are linked via a metal or other atom have been documented.

The first discotic twin based on benzene core was introduced by Lillya and Murthy[5] and later Zamir *et al*. also prepared similar benzene-based *dimers*.[6]

1a; n = 4
1b; n = 6
1c; n = 8
1d; n = 10
1e; n = 12
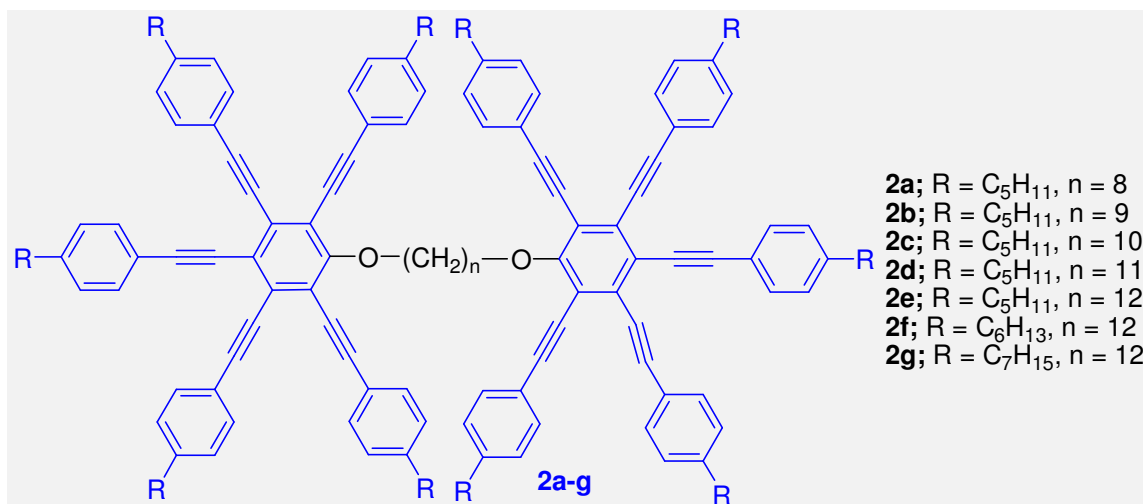**1f**; n = 18

1a-f
R = C$_6$H$_5$CO
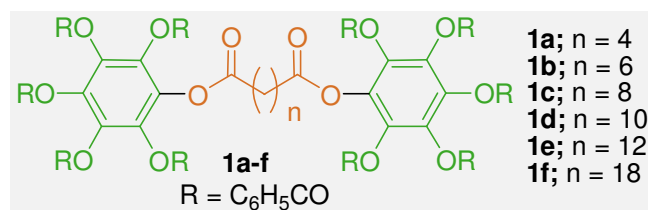
All the prepared *dimers* have heptanoyloxy periphery while the spacer length was varied from 4 carbons to 18 carbons. On increasing the spacer length, the tendency of the symmetrical dimer to display liquid crystallinity was increasing. Higher homologues of the dimer series **1d-f,** having ten or more carbon atoms in the spacer, exhibited mesomorphic behavior. Derivatives with smaller spacer **1a-c** failed to show liquid crystalline behavior. Whereas the compound **1d** and **1e** with decamethylene and dodecamethylene spacer showed rectangular mesophase, the longest spacer derivative **1f** displayed a hexagonal stacking of molecules. The thermal stability of the mesophase of these *dimers* **1d, 1e** was found to be greater than their monomeric counterpart. Thus, it was concluded that if the spacer is sufficiently long, discotic *dimers* can arrange themselves in columns. If the spacer length is about the twice or longer the length of peripheral chains, very similar mesophase are obtained as for the monomers.

Hexaalkynylbenzenes or multiynes are well-known discotic nematic liquid crystals. By connecting two bulkier pentaynes via a proper spacer may restrict the free rotation of monomesogenic units around the long axis of dimer molecule and, therefore, may induce biaxial nematic mesophase in such dimeric systems. This prompted Praefcke and co-workers

[5] C. P. Lillya, Y. L. N. Murthy, *Mol. Cryst. Liq. Cryst.*, *2*, 121, **1985**.
[6] S. Zamir, E. J. Wachtel, H. Zimmermann, S. Dai, N. Spielberg, R. Poupko, Z. Luz, *Liq. Cryst.*, 23, 689, **1997**.

to design and synthesize dimer of radial pentayne **2a**.[7] Subsequently many other related *dimers* were prepared and characterized.[8]

2a; R = C$_5$H$_{11}$, n = 8
2b; R = C$_5$H$_{11}$, n = 9
2c; R = C$_5$H$_{11}$, n = 10
2d; R = C$_5$H$_{11}$, n = 11
2e; R = C$_5$H$_{11}$, n = 12
2f; R = C$_6$H$_{13}$, n = 12
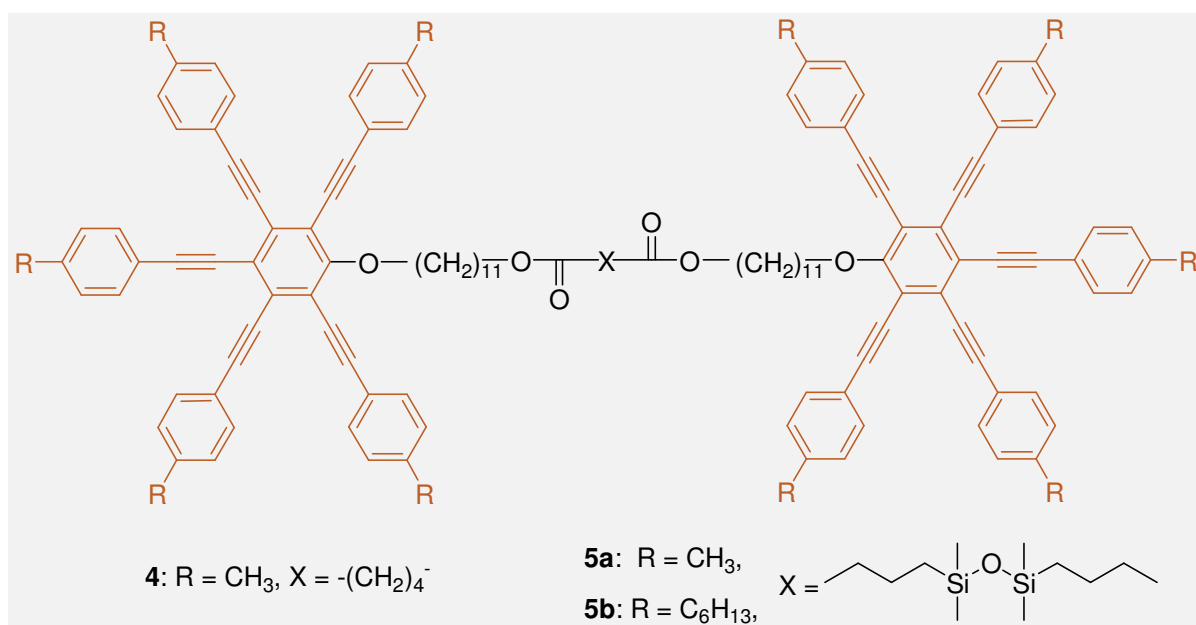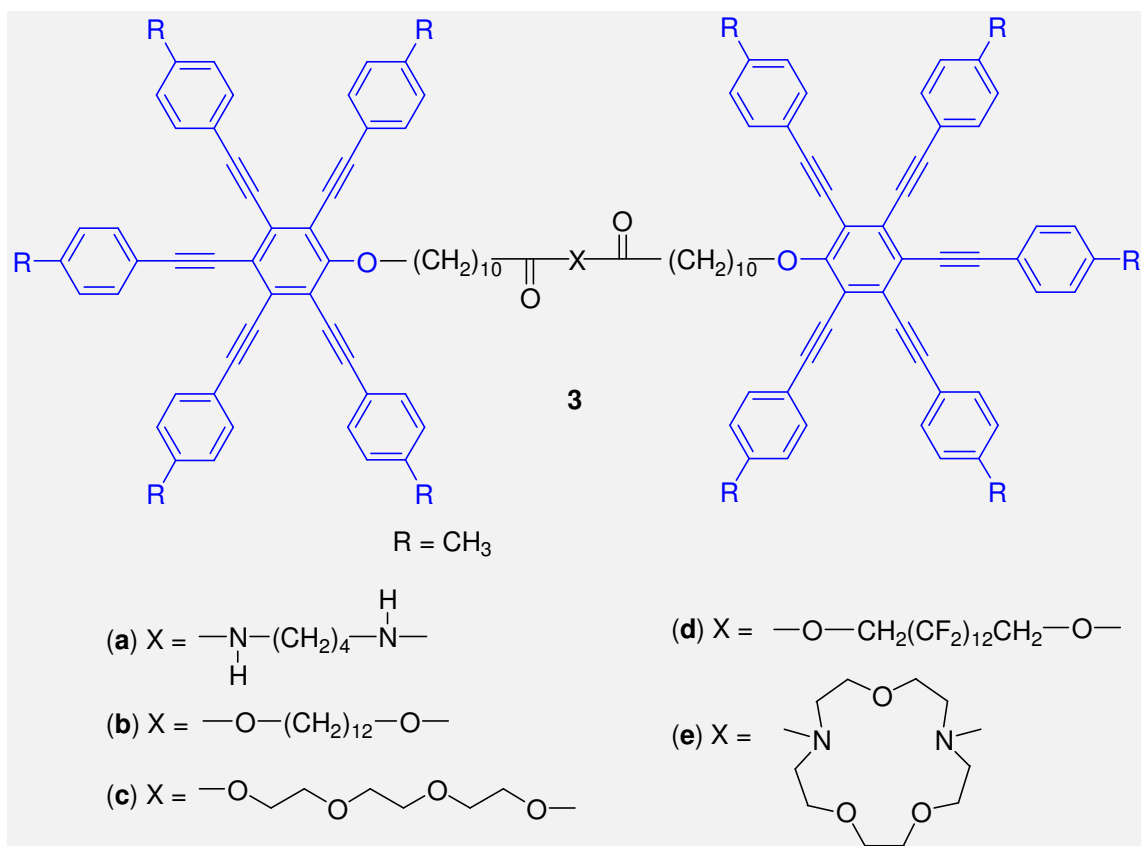2g; R = C$_7$H$_{15}$, n = 12

2a-g

All *dimers* displayed discotic nematic phase. The dyads with short spacer **2a**, **2b** showed very narrow or unstable mesophase. The mesophase range was comparatively broader for *dimers* **2c-e** with longer spacer. The clearing temperatures of twins **2a-e** show significant odd-even effect. For a constant spacer length (compare **2e, f, g**), the length of peripheral chain had reciprocal effect on crystalline-to-nematic point, clearing temperature, as well as the mesophase range.

Kouwer *et al*. used a spacer having ester group along with some other moieties as a part of linker for connecting two pentaynes.[8f,g] Introduction of ester or amide linkage in spacer tends to an increase in melting as well as clearing temperature. The dimer **3a** exhibits highest value of melting as well as isotropic temperature. This is most likely because of hydrogen bonding caused by amide linkage. Insertion of siloxane unit in the middle of spacer causes a significant decrease in transition temperatures. The peripheral methyl group substituted

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[7] K. Praefcke, B. Kohne, D. Singer, D. Demus, G. Pelzl, S. Diele, *Liq. Cryst.*, 7, 589, **1990**.

[8] (a) K. Praefcke, B. Kohne, B. Gundogan, D. Singer, D. Demus, S. Diele, G. Pelzl, U. Bakowsky, *Mol. Cryst. Liq. Cryst.*, 198, 393, **1991**; (b) M. Langner, K. Praefcke, D. Kruerke, G. Heppke, *J. Mater. Chem.*, 5, 693, **1995**; (c) C. J. Booth, D. Kruerke, G. Heppke, *J. Mater. Chem.*, 6, 927, **1996**; (d) J. Contzen, G. Heppke, H. S. Kitzerow, D. Kruerke, H. Schmid, *Apply. Phys. B*, 63, 605, **1996**; (e) J. S. Patel, K. Praefcke, D. Singer, M. Langner, *Apply. Phys. B,* 60, 469, **1995**; (f) P. H. J. Kouwer, W. F. Jager, W. J. Mijs, S. J. Picken, K. J. Shepperson, G. H. Mehl, *Mol. Cryst. Liq. Cryst.*, 411, 377, **2004**; (g) P. H. J. Kouwer, G. H. Mehl, *Mol.Cryst. Liq. Cryst.*, 411, 387, **2004**.

material **5a** was not liquid crystalline, however, replacement of methyl group with hexyloxy group (**5b**) allowed the occurrence of low temperature discotic nematic phase.

R = CH$_3$

(**a**) X = $-$N$-$(CH$_2$)$_4$$-N-$
        H   H

(**b**) X = $-$O$-$(CH$_2$)$_{12}$$-O-$

(**c**) X =

(**d**) X = $-$O$-$CH$_2$(CF$_2$)$_{12}$CH$_2$$-O-$

(**e**) X =

4: R = CH$_3$, X = -(CH$_2$)$_4$-

5a: R = CH$_3$,
5b: R = C$_6$H$_{13}$,

X =

An anthraquinone-based symmetrical dimer **6** in which two pentasubstituted anthraquinone units were connected through methylene spacer was reported by Krishnan and Balagurusamy.[9] The dimer **6** was reported to exhibits two transitions, one at 147 °C and the other at 180.4 °C during the first heating. However, during the cooling cycle only one transition at 176.6 °C corresponding to isotropic to columnar phase appears. In the second heating run, the first transition shifts to 114.7 °C. The actual reason for the first transition is uncertain. X-Ray diffraction of the dimer **6** recorded at 125 °C showed features of hexagonal columnar mesophase.

6
R = C_5H_{11}, R_1 = 4-nitrobenzyl
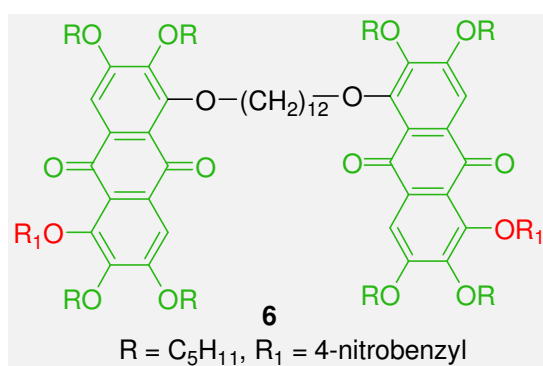
The pioneering work of Ringsdorf's group on the synthesis of triphenylene based polymeric side-chain and main-chain discotic liquid crystals[10,11] has also opened routes to triphenylene based discotic *dimers* and oligomers. They prepared mono- and di-functionalized triphenylenes using a statistical approach and converted them into side-chain and main-chain polymers. The potential utility of discotic *dimers*, oligomers and polymers has not yet been fully explored primarily due to the difficulties in preparing functionalized discotic precursors. However, in recent years, there have been many advances in the synthesis of mono-functionalized triphenylenes and consequently a number of triphenylene-based discotic *dimers*, oligomers and polymers have been realized.[12]

Contrary to benzene-based liquid crystalline dimer, which was simple and made of connecting two benzene discs with the help of spacer, the chemistry of triphenylene *dimers*

[9] K. Krishnan, V. S. K. Balagurusamy, *Liq. Cryst.*, 28, 321, **2001**.
[10] W. Kreuder, H. Ringsdorf, *Makromol. Chem. Rapid. Commun.*, 4, 807, **1983**.
[11] W. Kreuder, H. Ringsdorf, P. Tschirner, *Makromol. Chem. Rapid. Commun.*, 6, 367, **1985**.
[12] S. Kumar, *Liq. Cryst.*, 31, 1037, **2004**.

actually initiated with a rather complicated molecule in which the two triphenylene units were linked through a calamitic molecule. In order to prepare the chemical equivalence of the "Wheel of Mainz", **7**, Ringsdorf and co-worker connected two triphenylene units laterally to a calamitic mesogen.[13]

7: Cr 167 I

8: amorphous

9: Cr 72 LC 120 I

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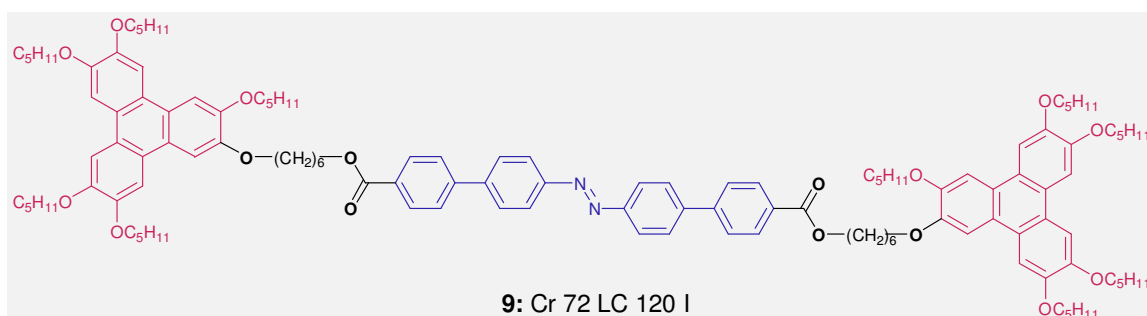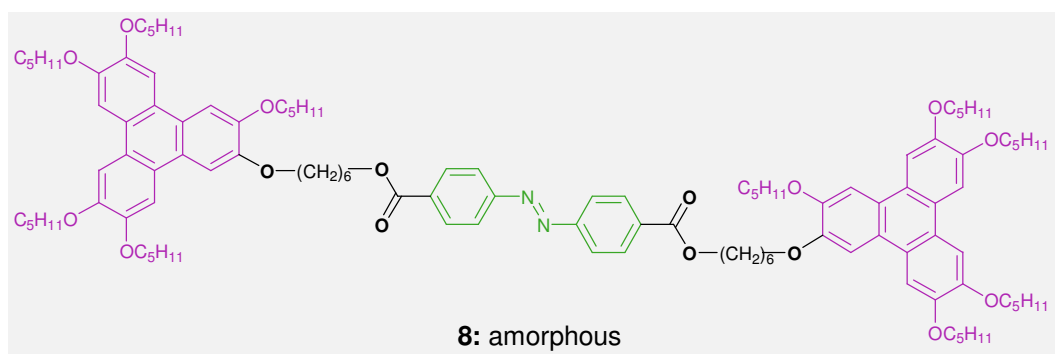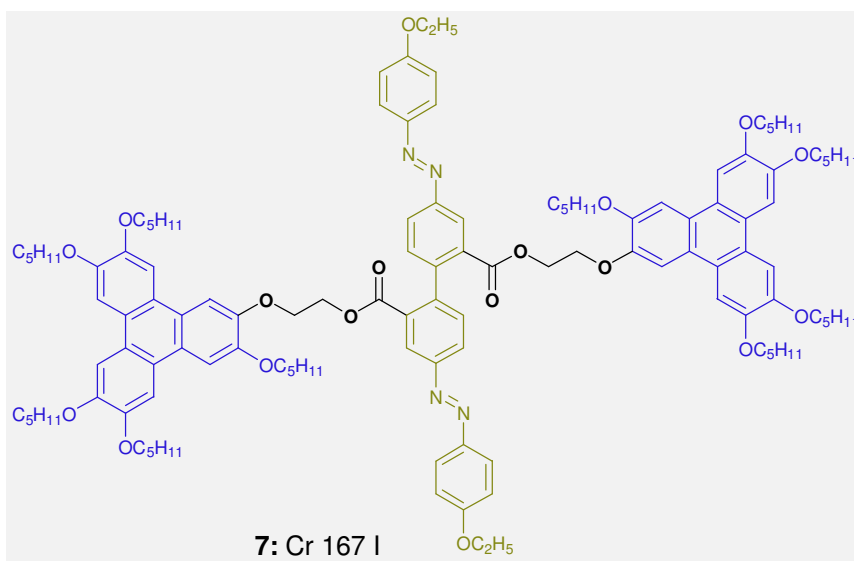
[13] W. Kreuder, H. Ringsdorf, O. H. Schonherr, J. H. Wendorff, *Angew. Chem. Int. Ed. Engl.*, 26, 1249, **1987**.

Compound **7** was found to be a spherolithic crystalline compound melting at 167 °C. Attaching the two triphenylene molecules linearly to a azobenzene moiety results in only an amorphous material **8**, but replacing the azobenzene by a mesogenic azobiphenyl moiety gave a liquid crystalline material **9**. It melts at 72 °C to a highly viscous mesophase and clear at 120 °C. The optical texture of this mesophase resembles with that of S_B mesophase. X-ray studies on this compound indicate a layer structure typical for smectic phases but in which the molecular disks are regularly stacked as observed for columnar phases.[13]

The most commonly prepared triphenylene based *dimers* contain two identical triphenylene moieties connected via a spacer. Often the spacer is a polymethylene chain,[14] but in some cases ester or amide linkage in the middle of the spacer or at the terminal positions have also been used.[14g,15]

|	
10a: R = C_4H_9, n = 6	**10g:** R = C_6H_{13}, n = 6
10b: R = C_4H_9, n = 8	**10h:** R = C_6H_{13}, n = 7
10c: R = C_5H_{11}, n = 8	**10i:** R = C_6H_{13}, n = 8
10d: R = C_6H_{13}, n = 1	**10j:** R = C_6H_{13}, n = 10
10e: R = C_6H_{13}, n = 3	**10k:** R = C_6H_{13}, n = 14
10f: R = C_6H_{13}, n = 5	
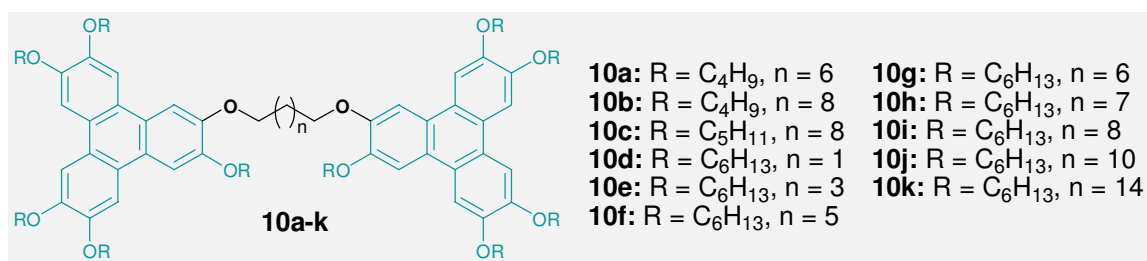
The length of spacer has a dramatic influence on the thermal behavior of *dimers* **10**. Symmetrical triphenylene *dimers* with short spacer are not liquid crystalline. Modeling studies suggest that the two triphenylene units are not coplanar due to steric crowding. Only those *dimers* in which the spacer is more than seven methylene units form columnar mesophase. In most of these *dimers* the columnar phase freezes into glassy state on cooling. The stability of the glassy state depends on the spacer length as well as on the symmetry of

[14] (a) S. Zamir, R. Poupko, Z. Luz, B. Huser, C. Boeffel, H. Zimmermann, *J. Am. Chem. Soc.*, 116, 1973, **1994**; (b) D. Adam, P. Schuhmacher, J. Simmerer, L. Haussling, W. Paulus, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf, D. Haarer, *Adv. Mater.*, 7, 276, **1995**; (c) N. Boden, R. J. Bushby, A. N. Cammidge, P. S. Martin, *J. Mater. Chem.*, 5, 1857, **1995**; (d) S. Kumar, P. Schuhmacher, P. Henderson, J. Rego, H. Ringsdorf, *Mol. Cryst. Liq. Cryst.,* 288, 211, **1996**; (e) A. Bacher, I. Bleyl, C. H. Erdelen, D. Haarer, W. Paulus, H. W. Schmidt, *Adv. Mater.,* 9, 1031, **1997**; (f) A. M. Van de Craats, L. D. A. Siebbeles, I. Bleyl, D. Haarer, Y. A. Berlin, A. A. Zharikov, J. M. Warman, *J. Phys. Chem. B.*, 102, 9625, **1998**; (g) N. Boden, R. J. Bushby, A. N. Cammidge, A. El – Mansoury, P. S. Martin, Z. Lu, *J. Mater. Chem.*, 9, 1391, **1999**.
[15] (a) S. Kumar, M. Manickam, H. Schonherr, *Liq. Cryst.*, 26, 1567, **1999**; (b) M. Manickam, A. Smith, M. Belloni, E. J. Shelley, P. R. Ashton, N. Spencer, J. A. Preece, *Liq. Cryst.*, 29, 497, **2002**; (c) W. Kranig, B. Huser, H. W. Spiess, W. Kreuder, H. Ringsdorf, H. Zimmermann, *Adv. Mater.*, 2, 36, **1990**.

the molecule. The non-symmetrical *dimers* usually give longer-lived glasses. As the length of linking chain increases, in general, the lifetime of the glassy state decreases.[14g]

Kimura *et al*. have designed and synthesized five novel triphenylene twins. In these *dimers*, the two triphenylene cores were connected with the help of flexible ethylene oxide spacer.[16]

11a: n = 3
11b: n = 4
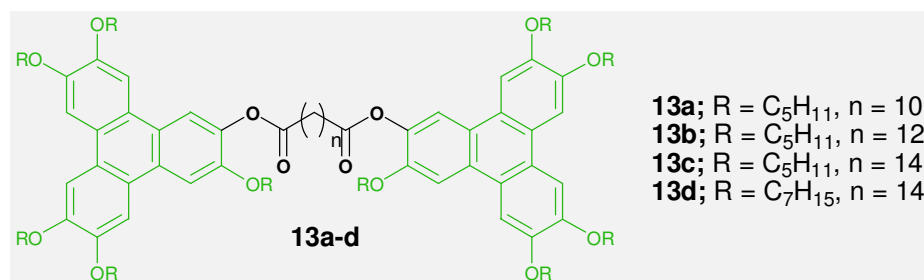**11c:** n = 5
11d: n = 6
11e: n = 8
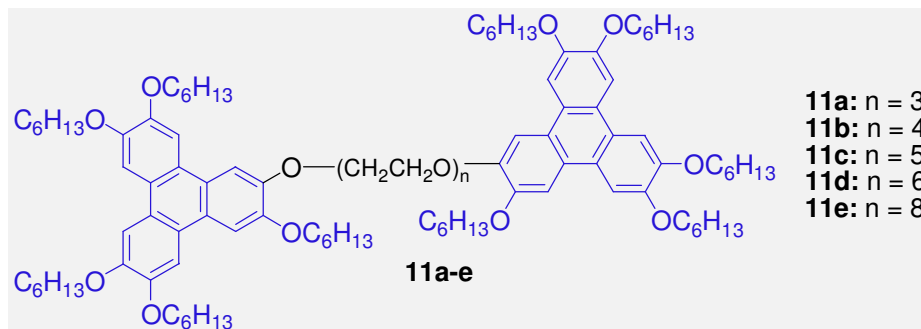
11a-e

The liquid crystallinity of these triphenylene-oligo(ethylene oxide)-triphenylene *dimers* **11a-e** was notably affected by the length of ethylene oxide spacer. The compound **11a** having the smallest spacer displayed monotropic hexagonal columnar phase. On second heating this compound melted to isotropic phase at 77 °C, while on cooling the mesophage appears at 54 °C. The compounds **11b** and **11c** with medium spacer length showed enantiotropic hexagonal columnar mesophase. These materials exhibited the mesophase from 50 °C to 93 °C. Contrary to this, higher homologues **11d, e** failed to exhibit any liquid crystalline property.

Boden and co-workers reported another symmetrical dimer **12** which differ from the above twins in the sense that in **12** instead of five long alkoxy chains in the monomer, one peripheral chain is only a short methoxy group. On heating, this compound shows a crystals to isotropic transition at 112 °C, but on cooling exhibits a monotropic columnar phase at 98 °C that persists down to a glass transition at 33 °C.[14c-g]

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16 M. Kimura, M. Moriyama, K. Kishimoto, M. Yoshio, T. Kato, *Liq. Cryst.*, 34, 107, **2007**.
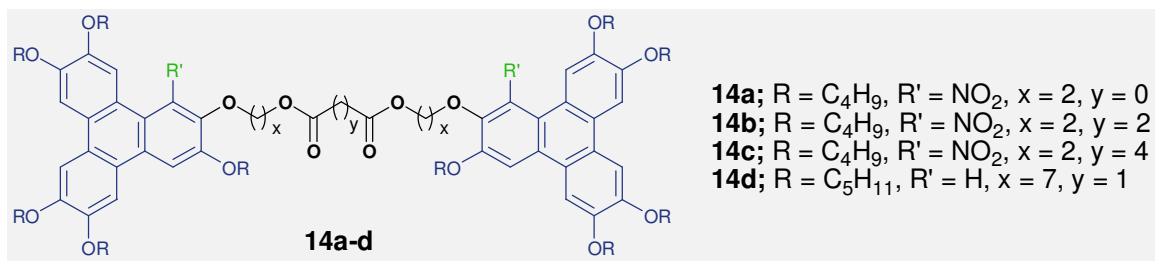
12: n = 8, Cr (98 Col$_h$ 33 g) 112 l
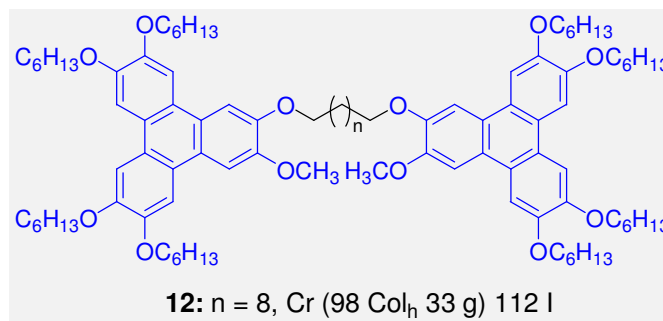
Four symmetrical triphenylene *dimers* **13a-d** in which two pentaalkoxytriphenylene units are connected via ester linkage instead of ether linkage were reported by Kranig *et al*. in 1990.[15c] All the four compounds were reported to be liquid crystalline at room temperature. These *dimers* exhibit much broader mesophase range compared with the *dimers* linked via ether bridges.

13a; R = C$_5$H$_{11}$, n = 10
13b; R = C$_5$H$_{11}$, n = 12
13c; R = C$_5$H$_{11}$, n = 14
13d; R = C$_7$H$_{15}$, n = 14

13a-d

In an effort to enhance the fluorescence as well as the liquid crystallinity of triphenylene-based *dimers*, a number of monofunctionalized triphenylene-based discotics bearing conjugative electron-withdrawing or electron-donating groups attached directly to the core were prepared.[17] Three such nitro-functionalized triphenylene *dimers* **14a-c** have been prepared starting from 2-hydroxy-3,6,7,10,11-pentaalkoxytriphenylene.[15a] A similar dimer **14d** but without having the nitro- group in the triphenylene unit was reported by Manickam *et al*.[15b]

---

[17] J. A. Rego, S. Kumar, H. Ringsdorf, *Chem. Mater*., 8, 1402, **1996**.

14a; R = C_4H_9, R' = NO_2, x = 2, y = 0
14b; R = C_4H_9, R' = NO_2, x = 2, y = 2
14c; R = C_4H_9, R' = NO_2, x = 2, y = 4
14d; R = C_5H_{11}, R' = H, x = 7, y = 1

14a-d

The spacer length of the diacid plays a crucial role in determining the phase behavior of these *dimers*. The presence of two or more methylene units in the spacer gives a liquid crystalline dimer with a very broad mesophase range, while spacers with less than two methylene units result in a monotropic mesophase (compound **14a**) or a crystalline phase (compound **14d**). This may be attributed to the steric hindrance of the two carbonyl groups, which is less pronounced if they are separated by two or more methylene units. The presence of the nitro group makes these materials yellow-coloured. Although, these nitro substituted *dimers* have very interesting properties, for example, stability of the mesophase at ambient temperature, very broad mesophase range, yellow colour and contain the highly polar nitro group in the core, because of synthetic problems they could not be prepared in large amount for various physical studies.

The formation of highly ordered self-assembled monolayers (SAMs) by mesogenic thiols, disulfides and thioethers on gold-covered substrates is well known.[18] Schonherr *et al*. studied the SAMs formation of the disulfide-bridged triphenylene dimer **15**. This waxy solid dimer shows an edge-on orientation on the gold surface.[19]

15: Waxy solid
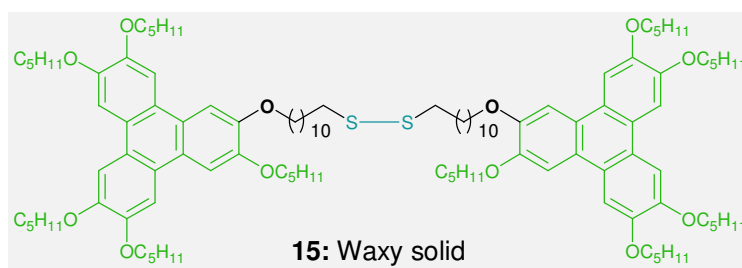
[18] A. Ulman, *Introduction to Ultrathin Films: From Langmuir-Blodgett Films to Self-Assembly*, Academic Press, Boston, **1991**.
[19] H. Schonheer, F. J. B. Kremer, S. Kumar, J. A. Rego, H. Wolf, H. Ringsdorf, M. Jaschke, H. J. Butt, E. Bamberg, *J. Am. Chem. Soc.*, 118, 13051, **1996**.

Recently, a triphenylene-based symmetrical dimer **16**, in which the two triphenylene moieties are connected via a methylene linker having Si-O-Si linkage in the middle of spacer, has been synthesized by Zelcer *et al.*[20] This dimer displayed hexagonal columnar mesophase in the range from 45 °C to 88 °C.

16: Cr 45.6 Col$_h$ 88 I
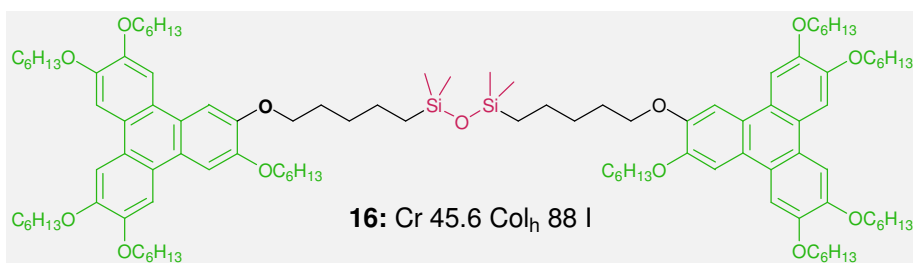
To explore the possibility that the insertion of C$_{60}$ into discotic systems may results in novel materials useful in device applications, Preece and co-worker synthesized the C$_{60}$ Bingel cyclopropanation-bistriphenylene adduct **17**,[15b] but as expected, the fullerene-bridged triphenylene dimer does not show any liquid crystalline properties.

17: Cr 58 I
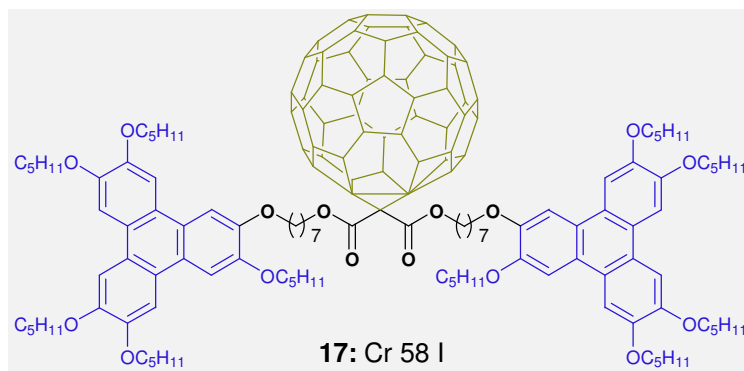
Hanack and co-workers have designed and synthesized four novel conjugated-bridged triphenylene-based *dimers* **18a-d** for the construction of organic light emitting diodes (OLEDs).[21]

[20] A. Zelcer, B. Donnio, C. Bourgogne, F. D. Cukiernit, D. Guillon, *Chem. mater.*, 19, 1992, **2007**.
[21] R. Freudenmann, B. Behnisch, M. Hanack, *J. Mater. Chem.*, 11, 1618, **2001**.

18a: R = CH$_3$
18b: R = CH$_2$CH(CH$_3$)$_2$
18c: R = CH$_2$CH$_2$CH(CH$_3$)$_2$
18d: R = C$_6$H$_{13}$

18a-d: Cr > 330 I
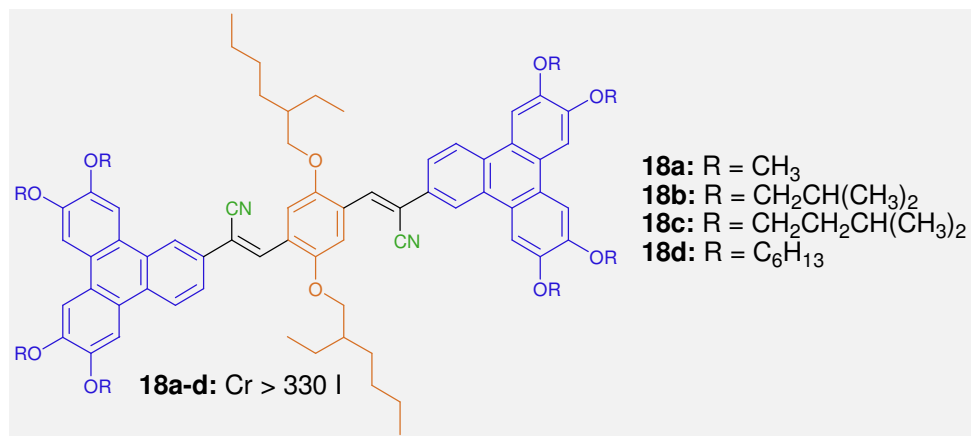
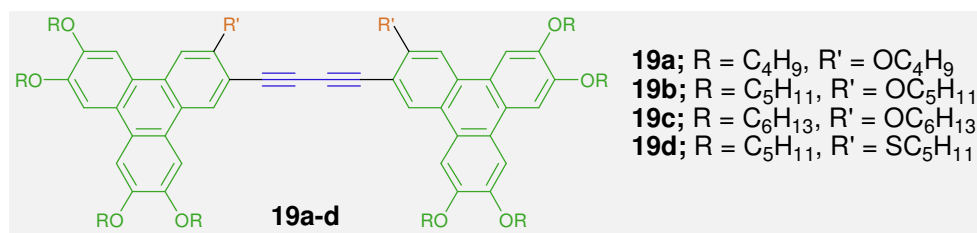All the four *dimers* were found not to be liquid crystalline and melted above 330 °C. They exhibit orange to red photoluminescence and a strong bathachromic shift of more than 250 nm when compared with a monomeric triphenylene system.

Discotic *dimers* in which two molecules are connected to each other via a long flexible alkyl chain spacer generally form columnar phases as the molecules have sufficient flexibility to stack in adjacent columns. Linking two discotic units via a short rigid spacer would be expected to give rise to steric hindrance arising from the overlapping or interdigitating of the aliphatic side chains, while the weak distortion in the planarity of the core would reduce the strong π-π interactions between the disks. Thus, the rigid molecules may adopt more or less parallel orientation but lose their long range translational order and, therefore, are likely to form discotic nematic phase. This concept has recently been realized by the synthesis of four triphenylene *dimers* **19a-d** in which two identical triphenylene units were connected via a rigid π-conjugated diacetylene spacer.[22]

19a; R = C$_4$H$_9$, R' = OC$_4$H$_9$
19b; R = C$_5$H$_{11}$, R' = OC$_5$H$_{11}$
19c; R = C$_6$H$_{13}$, R' = OC$_6$H$_{13}$
19d; R = C$_5$H$_{11}$, R' = SC$_5$H$_{11}$

19a-d

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[22] (a) S. Kumar, S. K. Varshney, *Org. Lett.*, 4, 157, **2002**; (b) S. Kumar, *Pramana*, 61, 199, **2003**; (c) S. Kumar, J. J. Naidu, *Liq. Cryst.*, 29, 899, **2002**.

These *dimers* form a discotic nematic mesophase over a wide temperature range. Compound **19d** differs from the other three in that one of the five alkoxy chains have been replaced by an alkylsulphanyl chain. This unusual triphenylene derivative, having three different types of peripheral chains was prepared from a triphenylene monomer having four alkoxy groups, a thioalkoxy and a free acetylene groups via a multi-step synthesis.[22c] This change destabilizes the nematic phase.

Although mercury-bridged linear calamitic *dimers* were described by Vorlander in 1923,[2] similar discotic structures appeared only in 2001. Two organometallic discotic liquid crystals **20a, b** in which a mercury atom is located at the centre of two substituted triphenylene molecules were prepared by Kumar *et al.*[23]
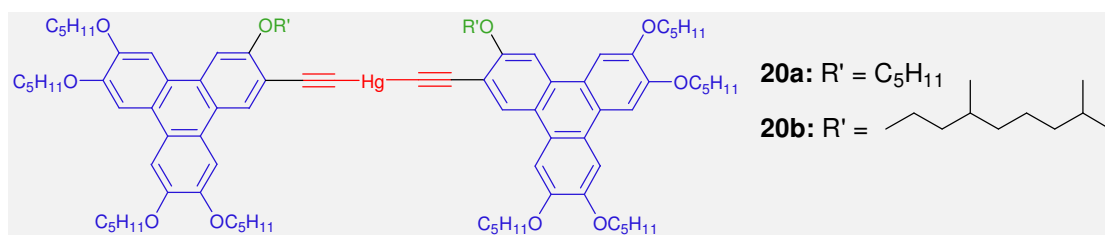

The crystalline compound **20a** transforms into a highly viscous but shearable fluid phase at about 150 °C. On further heating, this mesophase changes to an isotropic phase at about 210 °C but with decomposition. In order to reduce the clearing temperature, one of the normal alkyl chains was replaced by a branched chain (compound **20b**). This material on first heating shows a solid to solid transition at about 110 °C and this soft solid transforms into isotropic phase at 186 °C. On cooling the isotropic phase, a metastable nematic discotic phase appears at 185 °C. This monotropic mesophase has a strong tendency to crystallize which begins in the mesophase and is completed by 180 °C. On subsequent heating, the first transition at 110 °C was not observed and the crystal melts to isotropic liquid at 186 °C.
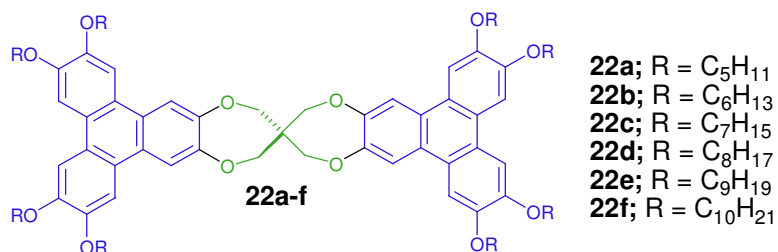
During the preparation of main-chain triphenylene polymers, Boden and co-workers isolated a low-molar mass compound that was identified as a cyclic dimer having structure

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[23] S. Kumar, S. K. Varshney, *Liq. Cryst.*, 28, 161, **2001**.

21a or **21b**. The similarity of the ^{1}H NMR spectrum of the dimer with that of polymer supports structure **21a** over **21b**. The dimer shows a mesophase range of 130–140 °C.[24]

21a   R = C_6H_{11}: Cr 130 Col 140 I   **21b**
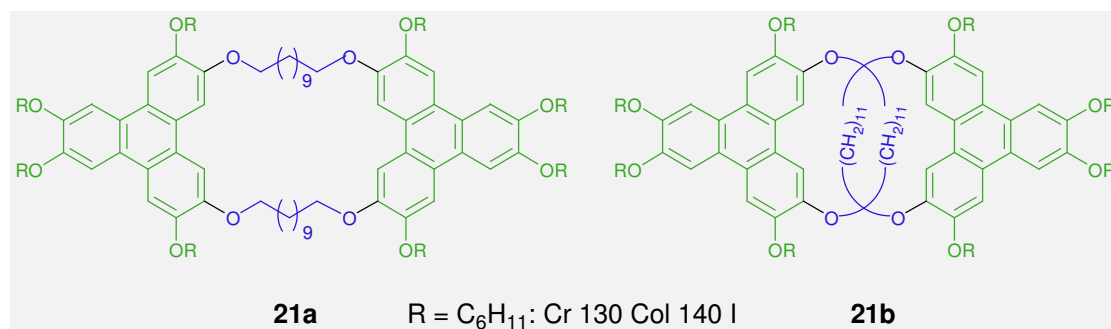
Schulte *et al*. prepared six novel triphenylene-based spiro-twins **22a-f** by condensing 1,2-dihydroxytriphenylenes with a tetrabromide.[25] Whereas the compounds **22a** and **22b** containing pentyloxy and hexyloxy chains, respectively showed only crystals to isotropic phase transition, the higher homologues **22c-f** displayed columnar mesophase.

22a-f

22a; R = C_5H_{11}
22b; R = C_6H_{13}
22c; R = C_7H_{15}
22d; R = C_8H_{17}
22e; R = C_9H_{19}
22f; R = $C_{10}H_{21}$

Mao *et al*. connected two triphenylene fragments covalently to a benzene ring via a carbamate linkage to produce the dimer **23**.[26] The high value of melting and clearing temperature can be attributed to the presence of hydrogen bonding which makes the molecular packing more efficient. In addition to the above phenomenon, hydrogen bonding supported this dimer to exhibit excellent film-forming property.

[24] N. Boden, R. J. Bushby, A. N. Cammidge, *J. Am. Chem. Soc.*, 117, 924, **1995**.
[25] J. L. Schulte, S. Laschat, V. Vill, E. Nishikawa, H. Finkelmann, M. Nimtz, *Eur. J .Org. Chem.*, 2499, **1998**.
[26] H. Mao, Z. He, J. Wang, C. Zhang, P. Xie, R. Zhang, *J. Luminescence,* 122-123, 942, **2007**.

23: Cr 177.7 Col 188 I
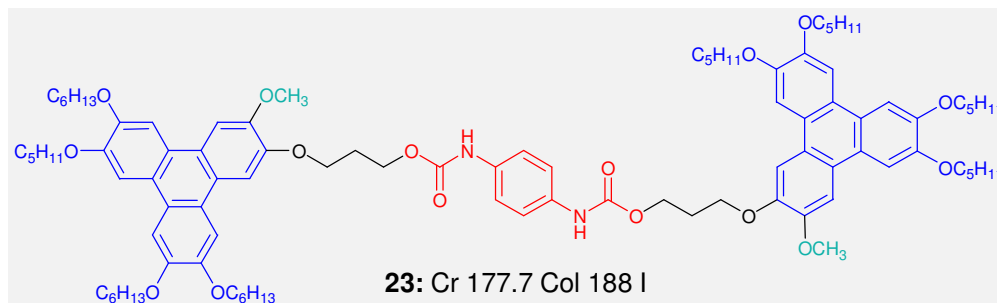
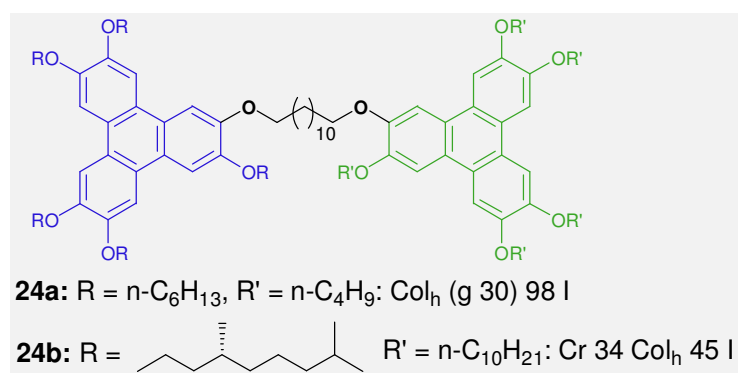The concept of reducing the molecular symmetry in order to reduce the melting point in monomeric DLCs has been adopted by several workers.[12] It is also known that the crystallization of glassy columnar phase shown by monomeric DLCs is retarded by reducing the symmetry of the disc.[14g] Two non-symmetric triphenylene-based *dimers* **24a** and **24b** have been reported.

24a: R = n-C_6H_{13}, R' = n-C_4H_9: Col_h (g 30) 98 I

24b: R = [structure] R' = n-$C_{10}H_{21}$: Cr 34 Col_h 45 I

In the dimer **24a,** a pentahexyloxytriphenylene unit was connected to a pentabutyloxytriphenylene unit via a polymethylene spacer. This compound shows a Col_h phase to isotropic phase transition at 98 °C. On cooling the columnar phase freezes into a glassy state at 30 °C.[14g] In compound **24b** a pentadecyloxytriphenylene subunit was tethered to a chiral pentakis(3,7-dimethyloctyloxy)triphenylene via a decyl spacer. This compound shows a crystal to columnar phase transition at 34 °C and clears at 45 °C in the first heating run of the DSC. On cooling the columnar phase appears at 44 °C and is stable to 0 °C. Despite the presence of a chiral triphenylene unit, no chiral mesophase was observed in this dimer.[27]

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[27] D. Hirst, S. Diele, S. Laschat, M. Nimtz, *Hel. Chimi. Acta.*, 84, 1190, **2001**.

The synthesis of dimer **25**, in which there is an amide group in the linking chain, was reported by Boden *et al.*[14g] It exhibits an enantiotropic columnar phase and forms a glass on cooling at about 30 °C. The glassy columnar state is stable for several months at room temperature.

25: Cr (g 30) 89 Col$_h$ 99 I
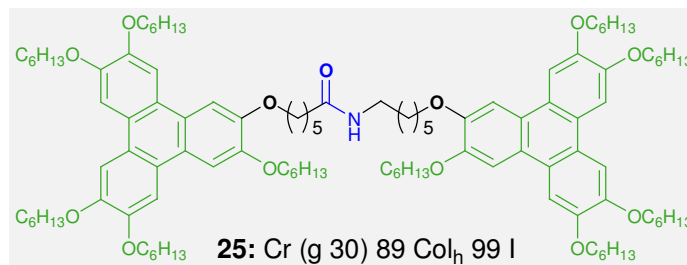
Percec and co-workers have reported synthesis and mesomorphic behavior of cyclotetraveratrylene (tetrabenzocyclododecatetraene) based symmetric dimer **26**.[28]

R = C$_7$H$_{15}$

26; Col1 81 Col2 122 Col$_h$ 136 I
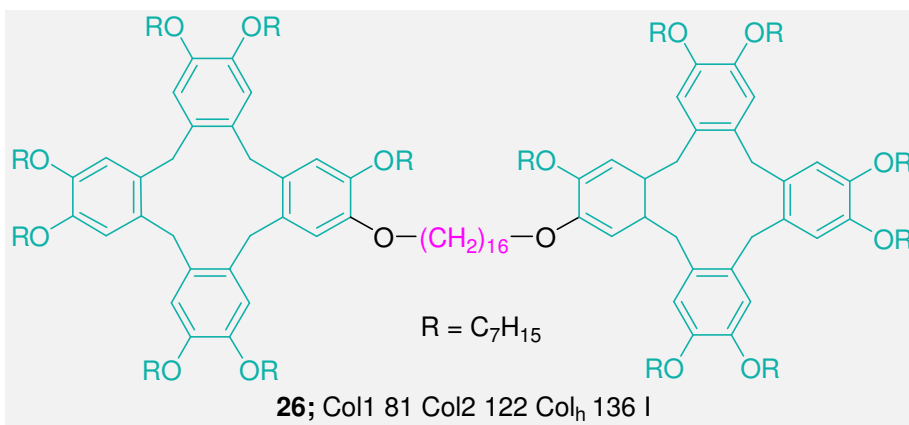
The dimer exhibits liquid crystalline behaviour at ambient temperature. It showed three enantiotropic columnar phases. The high temperature mesophase was characterized as hexagonal columnar but the nature of other two phases could not be revealed. The clearing point of this twin was lower than that of the corresponding monomeric compound.

Mullen and co-workers reported the synthesis of hexabenzocoronene (HBC) *dimers* **27** and **28**.[29] In the bishexa-*peri*-hexabenzocoronenyl **27**, two HBC rings were directly connected

[28] V. Percec, C. G. Cho, C. Pugh, D. Tomazos, *Macromol.*, 25, 1164, **1992**.
[29] S. Ito, T. Herwig, T. Bohme, J. P. Rabe, W. Rettig, K. Mullen, *J. Am. Chem. Soc.*, 122, 7698, **2000**.

to each other, while in the dihexa-*peri*-hexabenzocoronenyldodecane **28**, a long methylene spacer was used to tether two HBC disks.

R = C$_{12}$H$_{25}$

27

R = C$_{12}$H$_{25}$

28: Cr 53 Col$_h$ 370 I
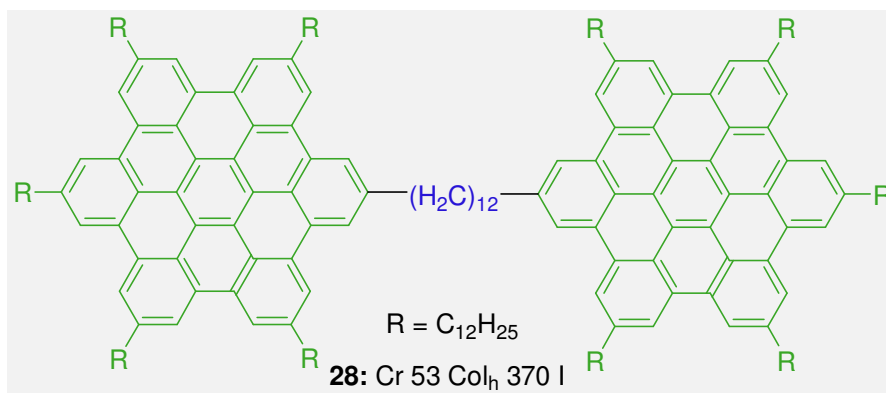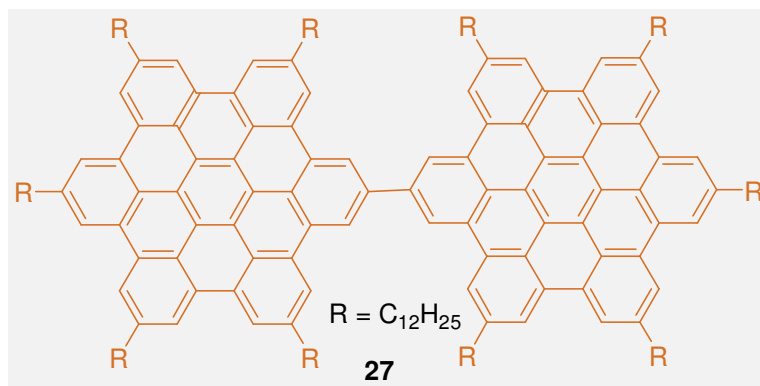
Both the HBC *dimers* were found to be liquid crystalline. Compound **27** showed a solid to mesophase transition at 124 °C on heating but no clearing transition was noticed up to decomposition. The liquid crystalline nature of **27** was confirmed by X-ray diffraction. An amazingly wider mesophase range of 317 °C was observed for the compound **28**. This dimer melts into ordered hexagonal columnar phase at 53 °C and goes to the isotropic phase at 370 °C.

In order to understand the influence of hydrogen bonding on the supramolecular order of HBC *dimers*, Mullen and co-workers prepared the *dimers* **29a, b** having amide and ester groups in the spacer.[30]

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[30] D. Wasserfallen, I. Fischbach, N. Chebotareva, M. Kastler, W. Pisula, F. Jackel, M. D. Watson, I. Schnell, J. P. Rabe, H. W. Spiess, K. Mullen, *Adv. Funct. Mater.*, 15, 1585, **2005**.

29a: X = NH
29b: X = O
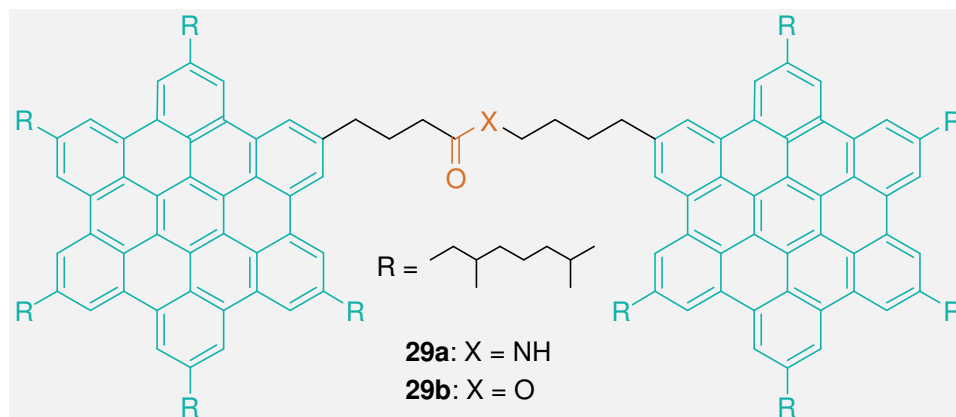
The dimer **29a** stayed in the pseudocrystalline phase over the whole temperature range of -100 to 300 °C. The compound **29b** was found to be liquid crystalline at room temperature with ordered hexagonal columnar arrangement. It did not give any sign of isotropization up to 300 °C on heating.

Watson *et al*. prepared cyclophane like *dimers* of HBC **30, 31**.[31] Both the cyclophane HBC *dimers* **30, 31** assembled in 2D hexagonal columnar mode. The DSC thermogram of **30** displayed a first order transition at 40 °C on heating. However a very weak second order glass transition at -10 °C was observed for compound **31.** The mesomorphic behaviour of these HBC *dimers* persist up to 400 °C on heating, as monitored by POM. Intracolumnar face-to-face stacking distance was found to be 3.6 Å. The dimer **31** which is not having any double bond in the spacer did not show any phase transition other than glass transition at -10 °C. It is notable that conversion of double bond (in **30**) to saturated single bond (in **31**) resulted in inhibition in bulk crystallization tendency of the rigid HBC cores.

[31] M. D. Watson, F. Jackel, N. Severin, J. P. Rabe, K. Mullen, *J. Am. Chem. Soc.*, 126, 1402, **2004**.

R = [structure]   **30**   **31**
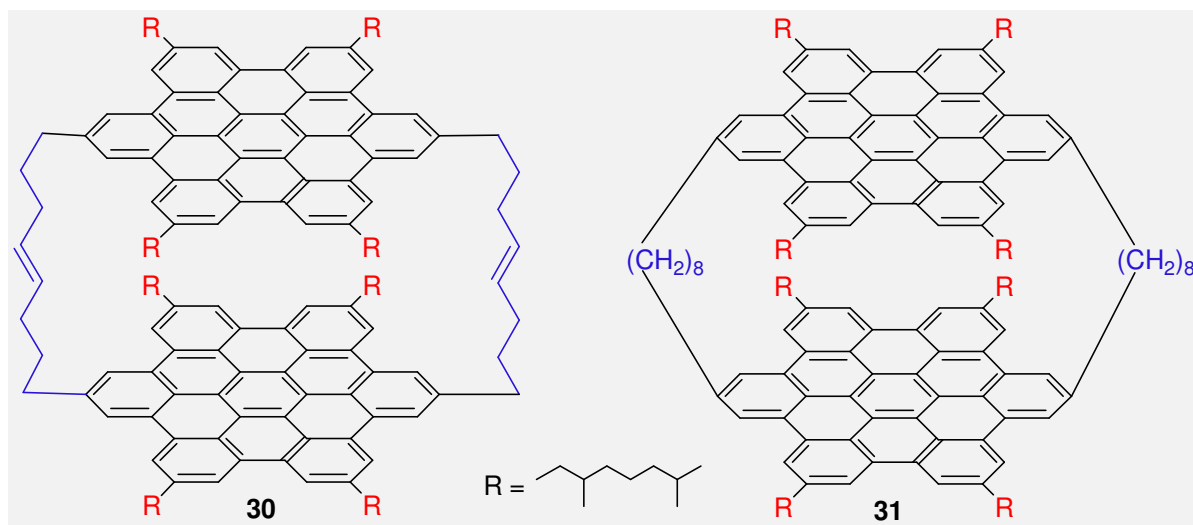
2.4.   Objective

A literature survey reveals that, although a variety of discotic *dimers* with *flexible* alkyl spacers are known, the effect of *flexible-rigid*-mixed spacer and relative orientation of mesogenic groups on the mesomorphic properties has not been well established. Therefore, the objective of the present synthetic work was to examine the effect of variation of the relative orientation of two mesogenic moieties around the benzene ring on the mesophase behavior of *dimers*. Additionally, in order to understand the structure–property relationships, we changed the lengths of the spacer, the relative proportion of rigid-to-flexible part in spacer and the type of linkage group also. Following molecular architectures were designed to execute this idea.

X = -O-   or   -COO-
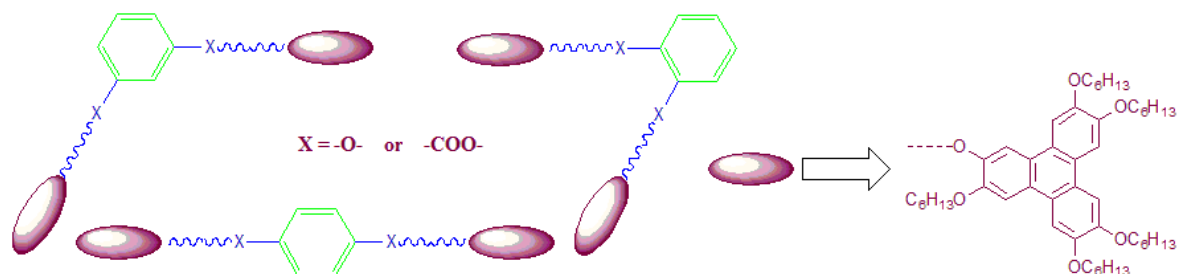
2.5. Synthesis of monohydroxypentaalkoxy triphenylene

Monohydroxytriphenylene **35** was prepared following literature methods[32] as described in the experimental part (Scheme 1).
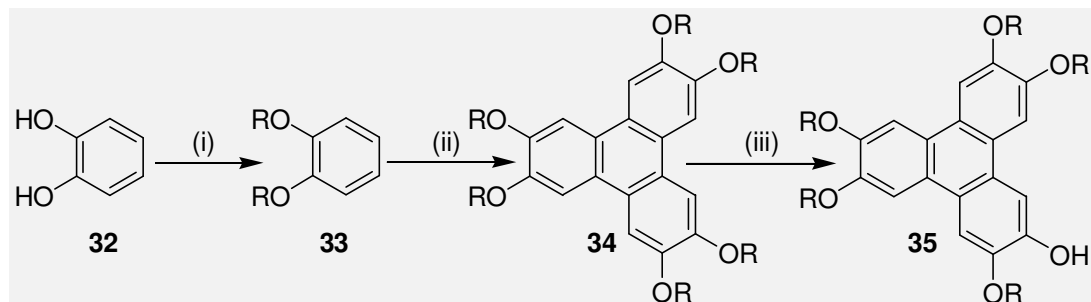
Scheme 1. Synthetic route for monohydroxytryphenylene. (i) RBr, K_2CO_3, Ethyl methyl ketone; (ii) $FeCl_3$, CH_2Cl_2; (iii) Cat-B-Br, CH_2Cl_2.

The synthesis of triphenylene starts from catechol. Two fold alkylation of catechol **32** in the presence of potassium carbonate in ethyl methyl ketone gives dialkoxybenzene **33**. Oxidative trimerization of dialkoxybenzene **33** with $FeCl_3$ in presence of a catalytic amount of H_2SO_4 provides hexaalkoxytriphenylenes **34** in 63 % yield. Selective dealkylation of one of alkoxy group of **34** using B-bromocatecholborane furnished monohydroxytriphenylenes **35** in about 40 % yield.

2.6. Synthesis of *dimers* of ester series

Compound **36** was synthesized by the route shown in Scheme 1. Potassium carbonate mediated etherification of monohydroxytriphenylene **35** with 6-bromohexanol-1 in ethyl-methyl ketone furnished the desired intermediate **36**.

[32] (a) S. Kumar, M. Manickam, *Chem Commun.*, 1615, **1997**; (b) S. Kumar, M. Manickam, *Synthesis*, 1119, **1998**; (c) S. Kumar, J. J. Naidu, S. K. Varshney, *Mol. Cryst. Liq. Cryst.*, 411, 355, **2004**.
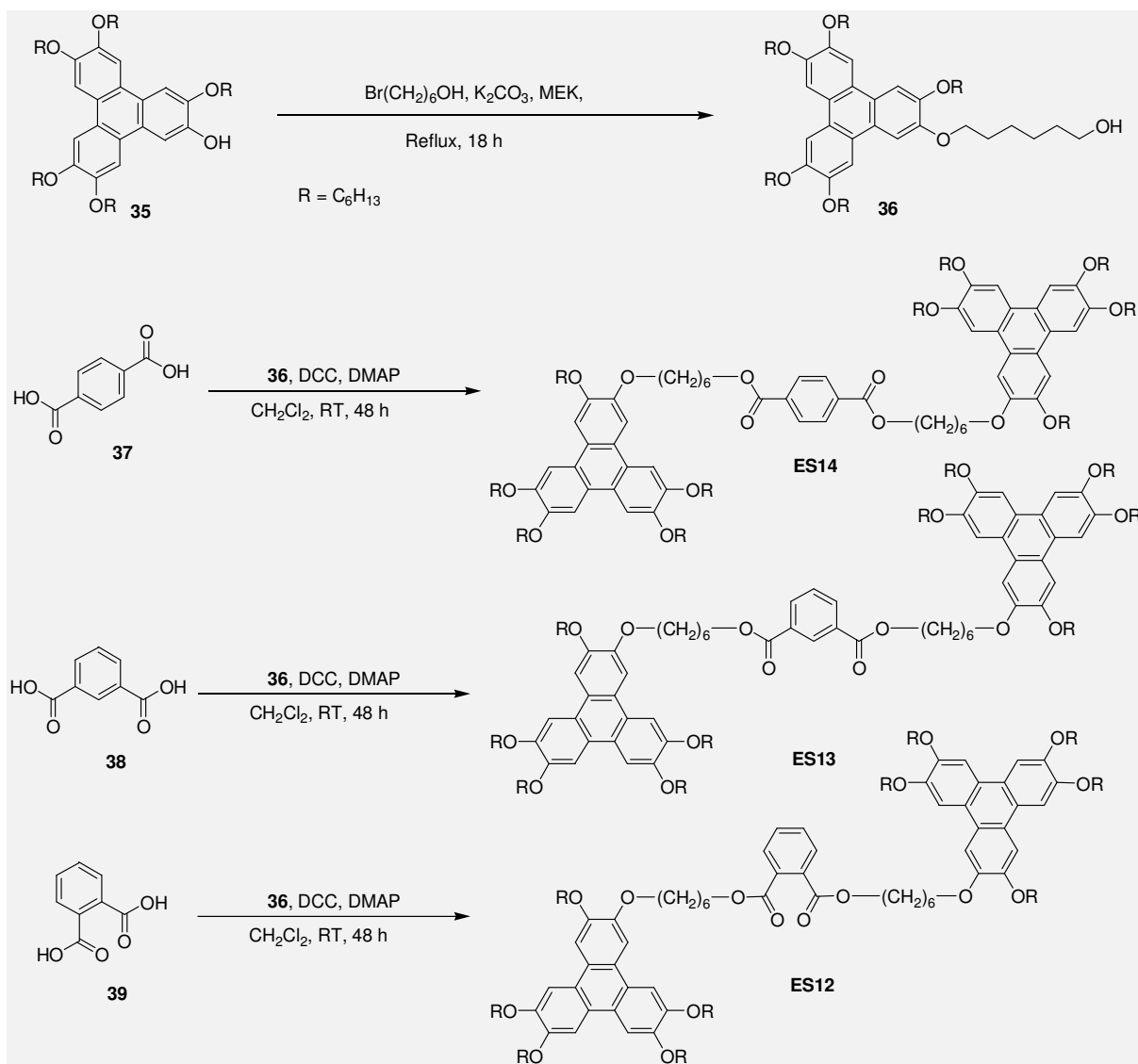
Scheme 2. Synthetic route for *dimers* of ester series.

The ester based *dimers* **ES14**, **ES13** and **ES12** were obtained by esterification of hydroxyl functionalized triphenylene **33** with benzene dicarboxylic acids **37** (terphthalic acid), **38** (isophthalic acid) and **39** (phthalic acid), respectively, in presence of N,N'-dicyclohexylcarbidimide (DCC) and catalytic amount of 4-dimethylaminopyridine (DMAP) in dry dicloromethane as a solvent. The details of procedure have been given in experimental section.

2.6.1. Characterization of *dimers* of ester series

All the *dimers* were purified by repeated column chromatography followed by crystallization and characterized from their ^{1}H NMR and elemental analysis. Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. ^{1}H NMR of dimers of ester series have been represented in Figures 3-5. Some of the important peaks (ppm values) are listed in Table 1.

Table 1. Selected ^{1}H NMR data of dimers of ester series (See the experimental part for detailed NMR data).

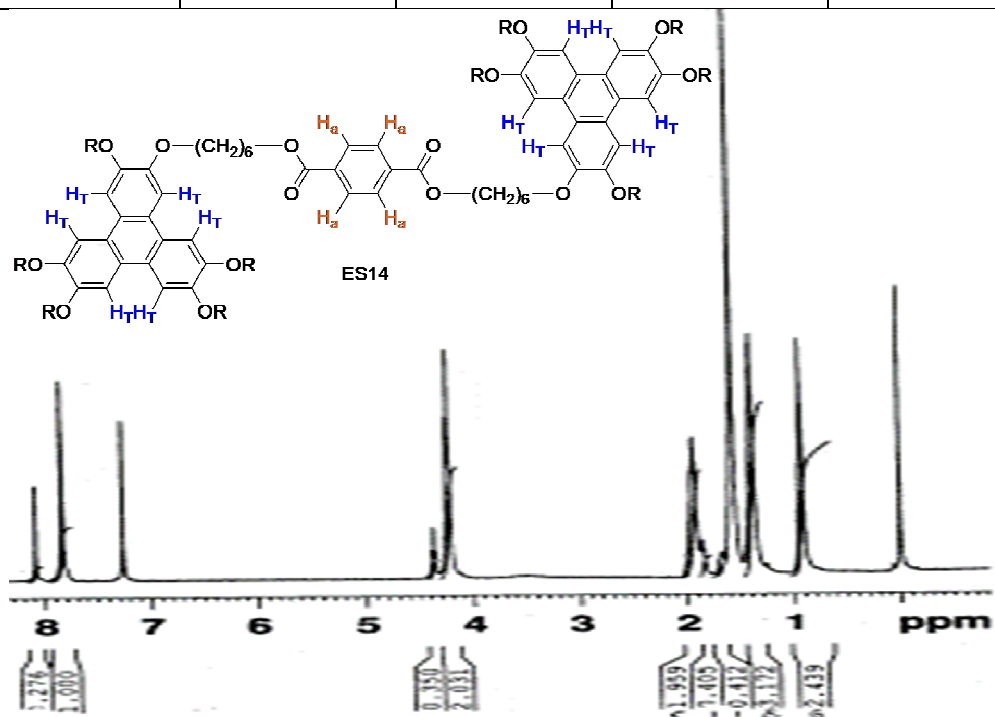|	H_T	H_a	H_b	H_c
ES14	7.83	8.08	---	---
ES13	7.82	8.7	8.2	7.47
ES12	7.81	7.68	7.48	---

Figure 3. ^{1}H NMR spectrum of the compound **ES14**.
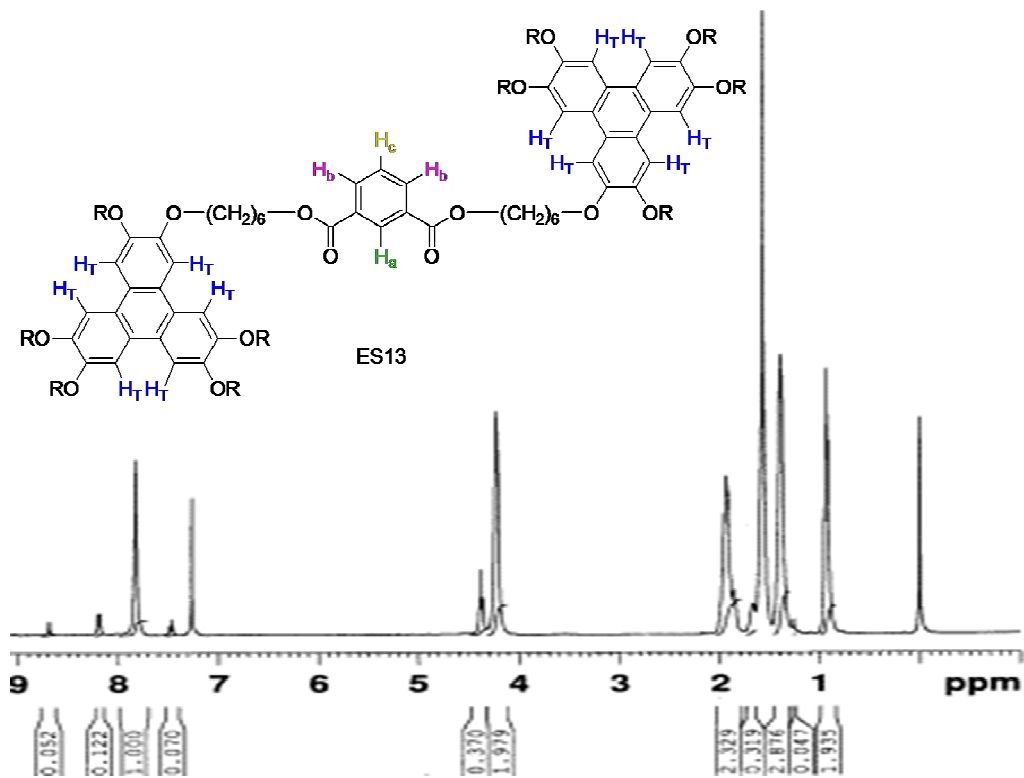
Figure 4. ^{1}H NMR spectrum of the compound **ES13.**
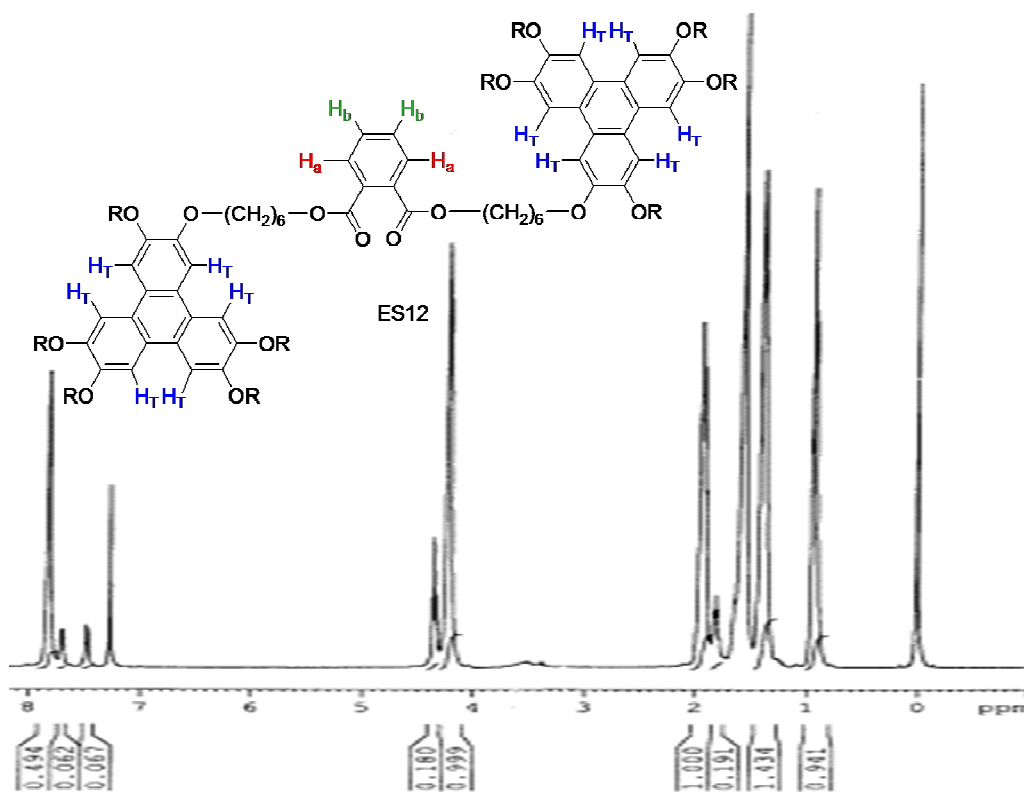
Figure 5. ^{1}H NMR spectrum of the compound **ES12.**

2.6.2. Thermal behavior of *dimers* of ester series

None of the compounds from *ester* series showed any liquid crystalline phase in its pure form. On heating, all the *dimers* exhibited isotropization above a certain temperature, and crystallized over a period of time (a week or more) on keeping the sample at room temperature. In DSC, these *dimers* did not show any transition up to room temperature in cooling scan. The isotropization temperature ranges in between 50-73 °C (Table 2).

Table 2: Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ/mol in parentheses) of dimers of *ester* series.

Compound/Mixture	First heating scan	First cooling scan
ES14	Cr 72.5 (79.38) I*	No transition
ES13	Cr 50.8 (76.28) I*	No transition
ES12	Cr 61.6 (77.37) I*	No transition

2.7. Synthesis of *dimers* of ether series

ω-bromo-substituted triphenylene **40** was prepared following the method described in the literature.[32] Potassium carbonate mediated etherification of monohydroxytriphenylene **35** with excess of 1, ω-dibromoalkane in ethyl-methyl ketone furnished the desired intermediate **40**. The synthesis of triphenylene-benzene-based ether series *dimers* is outlined in Scheme 3.
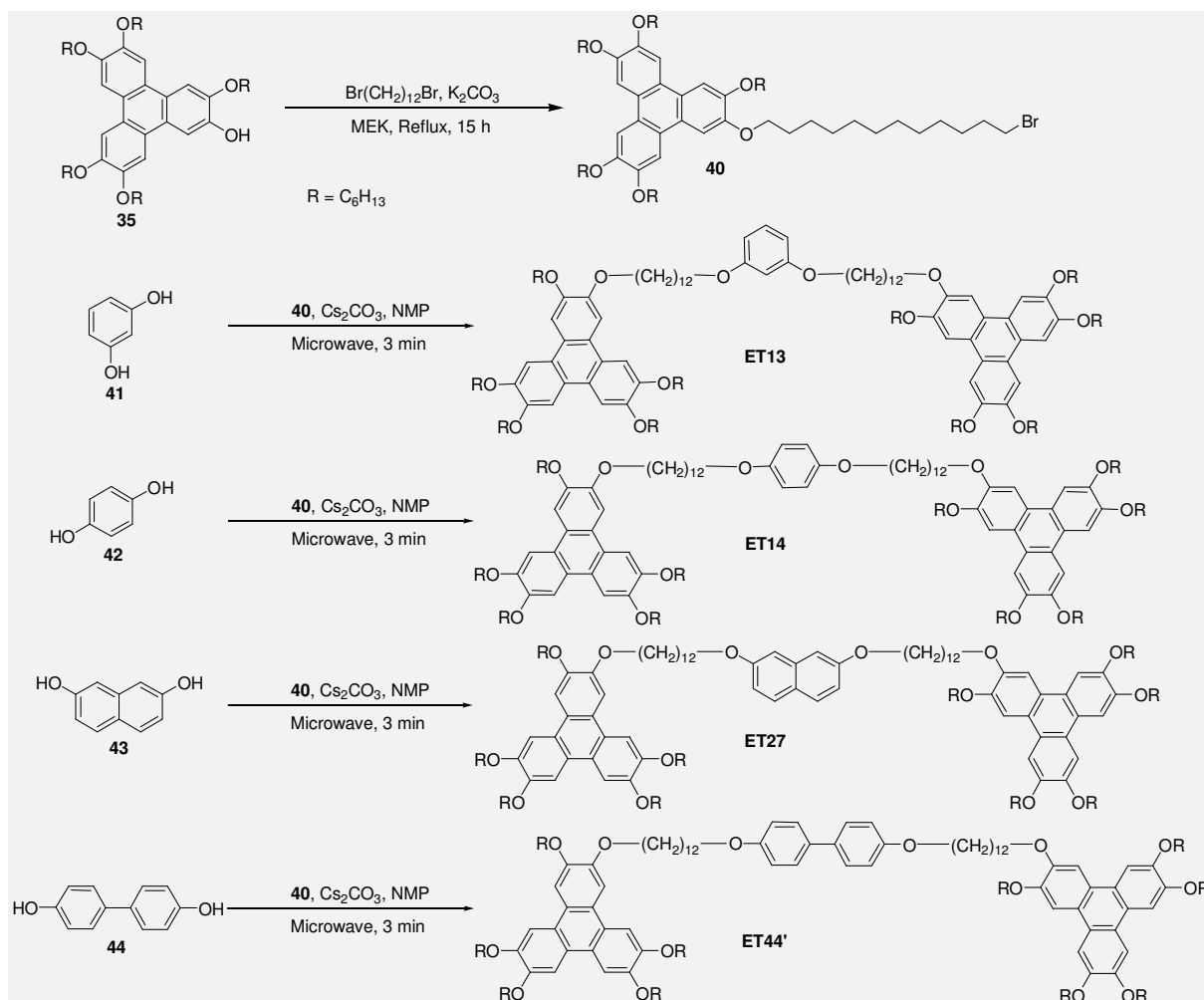
Scheme 3. Synthetic route for *dimers* of ether series.

The synthesis of triphenylene-benzene-based *dimers* of ether series **ET13**, **ET14**, **ET27** and **ET44′** involves caesium carbonate mediated alkylation of dihydroxy benzene based compounds **41** (resorcinol) and **42** (hydroquinone). Similarily compound **43** (2, 7-dihydroxynaphthalene) and **44** (4, 4′-dihydroxybiphenyl) were also prepared. The etherification was performed by irradiating a mixture of excess of ω-brominated triphenylene **40** with excess of caesium carbonate and **41** (or **42** or **43** or **44**) in N-methylpyrrolidone (NMP) under microwaves. The details of procedure have been given in experimental section.

2.7.1. Characterization of *dimers* of ether series

All the *dimers* were purified by repeated column chromatography followed by crystallization and characterized from their ^{1}H NMR and elemental analysis. Spectral data and elemental analysis of all the compounds were in good agreement with their structures, indicating the high purity of all the materials. ^{1}H NMR of dimers of ether series have been shown in Figures 6-9. Some of the important peaks (ppm values) are listed in Table 3.

Table 3. Selected ^{1}H NMR data of dimers of ether series (See the experimental part for detailed NMR data).

	H_T	H_a	H_b	H_c
ET13	7.83	7.14	6.46	---
ET14	7.83	6.8	---	---
ET27	7.83	6.98	7.01	7.63
ET44'	7.83	6.93	7.43	---
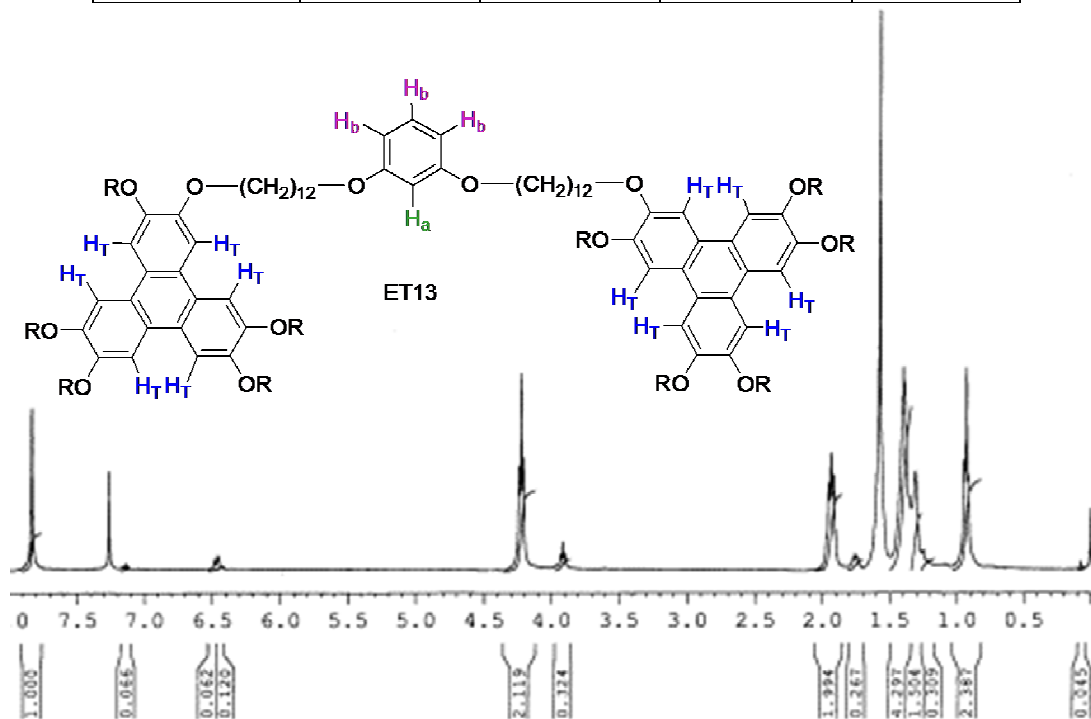
Figure 6. ^{1}H NMR spectrum of the compound **ET13.**
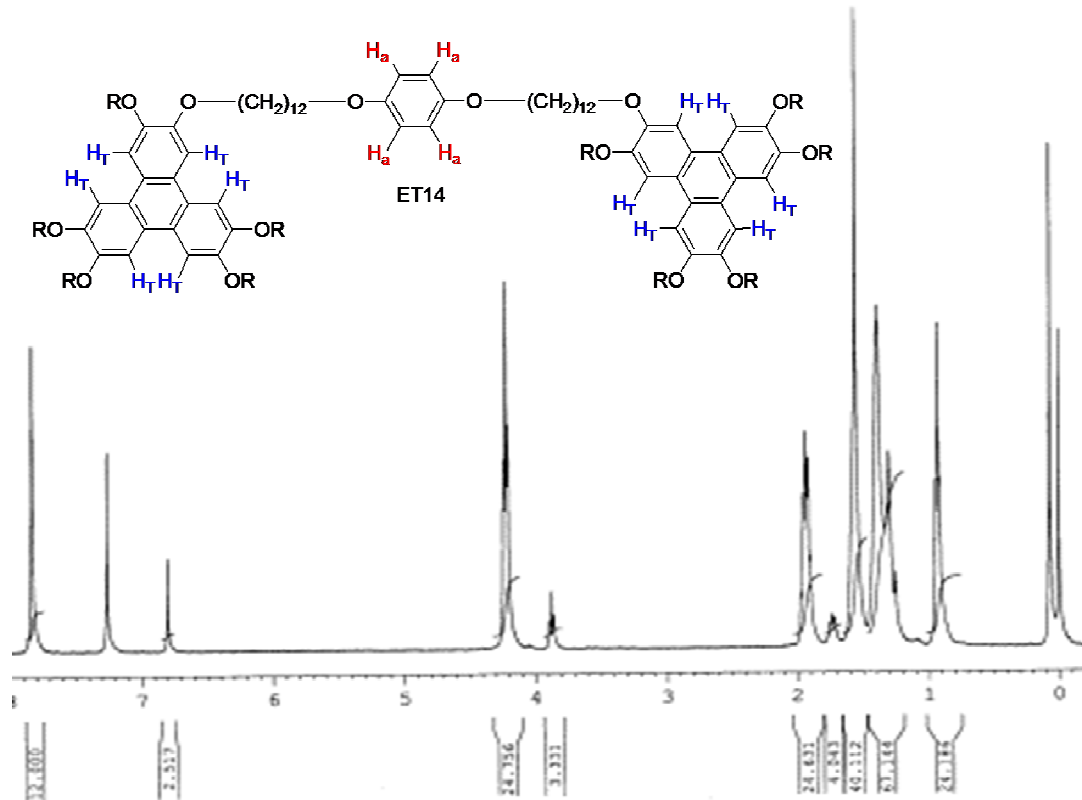
Figure 7. ^{1}H NMR spectrum of the compound **ET14.**
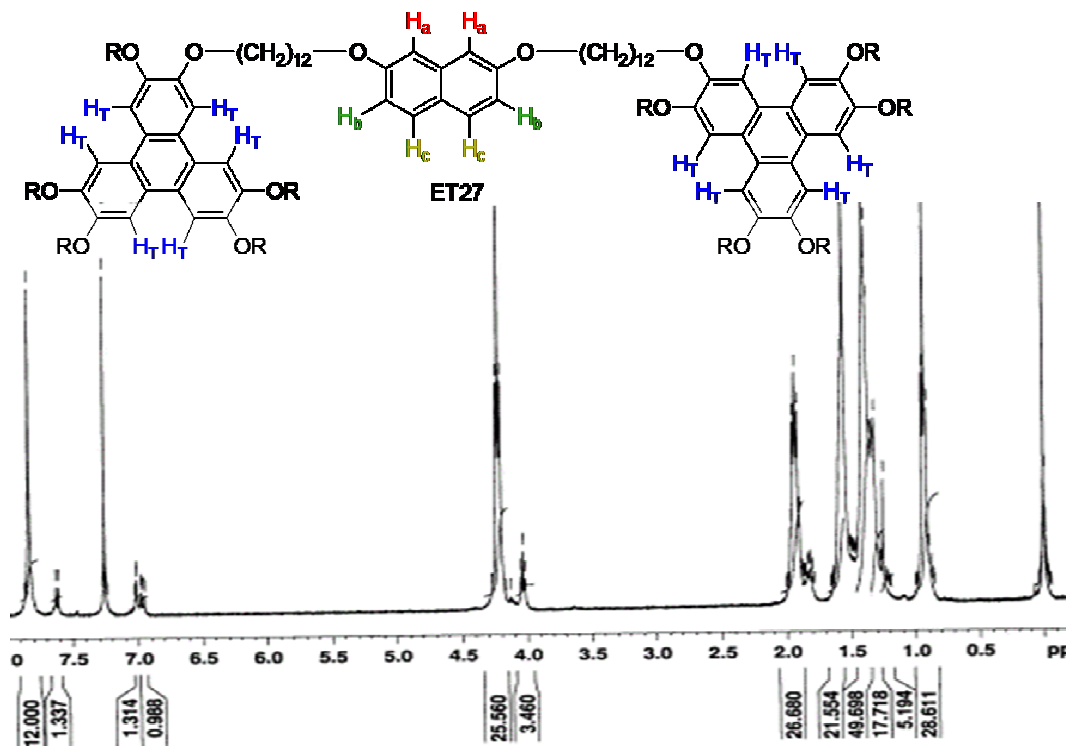
Figure 8. ^{1}H NMR spectrum of the compound **ET27.**
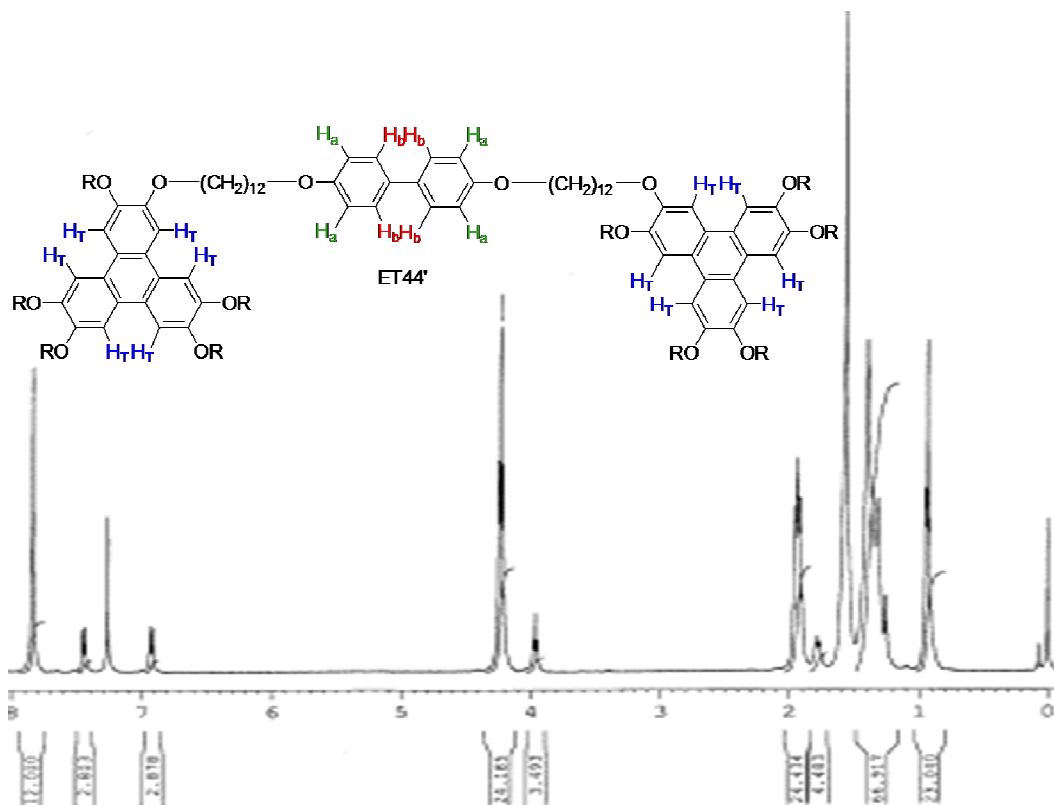
Figure 9. [^1]H NMR spectrum of the compound **ET44'.**

2.7.2. Thermal behavior of *dimers* of ether series

Similar to ester series, none of the compounds from *ether* series showed any liquid crystalline phase in its pure form. On heating, all the *dimers* exhibited isotropization above a certain temperature, and crystallized over a period of time (a week or more) on keeping the sample at room temperature. In DSC, these *dimers* did not show any transition up to room temperature in cooling scan. The isotropization temperature ranges in between 36-55 °C (Table 4). It is notable that the clearing point for *dimers* of *ether* series is less as compared to that of *dimers* having *ester* linkage.

Table 4: Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ/mol in parentheses) of dimers of *ether* series.

Compound/Mixture	First heating scan	First cooling scan
ET13	Cr 39 (39.43) I	No transition
ET14	Cr 36 (39.82) I	No transition
ET27	Cr 37 (52.9) I	No transition
ET44′	Cr 55 (47.2) I	No transition

2.8.   Mesophase induction via charge transfer complex formation

Mesomorphic properties of an organic material are governed by the shape of its constituent molecules and also by specific interactions of various kinds between them. Out of those specific interactions, charge transfer complexation has opened interesting prospects in research. Ringsdorf *et al.*, for the first time realized the approach of inducing columnar stacking interactions for the design of mesomorphic systems composed of disc or sheet shaped molecules.[33] They observed trinitrofluorenone (TNF)-induced columnar nematic and hexagonal columnar phases in amorphous side-chain triphenylene polymers and main-chain triphenylene polymers, respectively. Stabilization and extension of existing mesomorphic range due to charge transfer interaction induced by TNF has also been well explored in hexaethers and hexaesters of triphenylene.[33b,34] The isotropic transition temperature goes up to a maximum for a particular concentration on of electron acceptor, above which there occurs phase separation. Some previous investigations have been performed on charge transfer

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[33] (a) H. Ringsdorf, R. Wustefeld, E. Zerta, M. Ebert, J. H. Wendorff, *Angrew. Chem.,* 101, 934, **1989**; (b) H. Ringsdorf, R. Wustefeld, O. Karthaus, H. Bengs, M. Ebert, J. H. Wendorff, K. Praefcke, B. Kohne, *Adv. Mater.,* 2, 141, **1990**.

[34] (a) C. Destrade, P. Foucher, H. Gasparoux, H. T. Nguyen, A. M. Levelut, J. Malthete, *Mol. Cryst. Liq. Cryst.,* 106, 121, **1984**; (b) M. Ebert, G. Frick, C. Baehr, J. H. Wendorff, R. Wüstefeld, H. Ringsdorf, *Liq. Cryst.*, 11, 293, **1992**.

induced mesophase formation or stabilization in a binary mixture between triphenylene derivatives and TNF.[15c,34b,35] Similar TNF treatment experiments have been done with symmetrical and non-symmetrical radial multiynes.[34b,36] Triphenylene based donor-acceptor twin[37] donor-acceptor-donor triads[38] and donor-rod-acceptor triads[39] have been studied. Donor-acceptor dimer[40] and donor-rod-acceptor trimer[41] incorporating multiyne as electron rich and TNF as electron poor moiety have also been reported. Donor and acceptor units were found to intercalate within a column and the rod like unit was oriented more or less perpendicular to the column axis.

2.9. Preperation of charge transfer complexes of *dimers* with Trinitrofluorenone (TNF)

In order to increase molecular interactions and thus induce the mesomorphic behavior, we doped our dimer compounds with TNF in different molar ratios. Charge transfer complexes were prepared by mixing *dimers* with TNF in different molar proportions *i.e.* 2:1, 1:1, 1:2, 1:4 and 1:9 [TNF : dimer]. Calculated amount of TNF and dimer were dissolved in dry dichloromethane, both the colourless solutions were mixed, which resulted in deep brown colouration. The dichloromethane was then allowed to evaporate by leaving the solution to stand overnight and then final traces were removed under high vacuum to afford a dark brown solid.

2.9.1. Thermal behavior of charge transfer complexes

All the non-liquid crystalline *dimers* exhibit induced hexagonal columnar mesophase by charge transfer interactions in binary mixture with 2, 4, 7-trinitrofluorenone. None of the doped *dimers* showed any first order phase transition in DSC at 5°, 10° and 20 °C/min scan rates. However, the existence of liquid crystalline phase was confirmed by polarizing optical

35 W. Kraing, C. Boeffel, H. W. Spiess, *Liq. Cryst.*, 8, 375, **1990**.
36 (a) K. Praefcke, D. Singer, B. Kohne, M. Ebert, A. Liebmann, J. H. Wendorff, *Liq. Cryst.*, 110, 147, **1991**; (b) I. D. Fletcher, G. R. Luckhurst, *Liq. Cryst.*, 18, 175, **1995**; (c) D. Janietz, K. Praefcke, D. Singer, *Liq. Cryst.*, 13, 247, **1993**.
37 V. V. Tsukruk, D. H. Reneker, H. Bengs, H. Ringsdorf, *Langmuir,* 9, 2141, **1993**.
38 V. V. Tsukruk, H. Bengs, H. Ringsdorf, *Langmuir,* 12, 754, **1996**.
39 S. Mahlstedt, D. Janietz, A. Stracke, J. H. Wendorff, *Chem. Commun.,* 15, **2000**.
40 D. Janietz, *Chem. Commun.,* 713, **1996**.
41 S. Mahlstedt, D. Janietz, C. Schmidt, A. Stracke, J. H. Wendorff, *Liq. Cryst,,* 26, 1359, **1999**.

microscopy and X-ray diffraction. The textures were obtained by heating the binary mixture above isotropic transition temperature and subsequent cooling with cooling rate of 2-4 °C/min. During the heating, we observed only softening of materials with increasing temperature without any textural change. However, the mesophase texture appeared on cooling with 4-10 °C supercooling. All the virgin compounds as well as TNF complexes of ester series displayed higher clearing temperatures compared to ether series. Upon cooling from the isotropic phase, mesophase textures appear with very week birefringence. Shearing the sample in liquid crystalline state, increases the birefringence significantly. Such phenomenon indicates homeotropic alignment of columns perpendicular to the substrates.[42] The size of the domains depends on the cooling rate. A slower cooling rate results in larger optical domain. From optical textures given in Figure 10-14, it is clear that the average domain size decreases and becomes less defined on increasing dimer concentration in the binary mixture with TNF. The mesophase to isotropic transition temperature is also affected by TNF proportion in the binary mixture, which is greater for higher TNF concentration. The maximum clearing points and therefore the maximum stability is found for 1:2 molar composition (66% TNF *i.e.* one TNF molecule for per triphenylene disk) of dimer and TNF.

Table 5: Phase transition temperatures (peak, °C) and associated enthalpy changes (kJ/mol in parentheses) of *dimers* and their composites**.**

Compound/Mixture	First heating scan	First cooling scan
ES14	Cr 72.5 (79.38) I[*]	No transition
ES13	Cr 50.8 (76.28) I[*]	No transition
ES12	Cr 61.6 (77.37) I[*]	No transition
ES12:TNF[1:1]	Cr 190 I[**]	I 186 Col_h[**]

[42] T. S. Perova, J. K. Vij, *Adv. Mater.*, 7, 919, **1995**.

ES12:TNF[2:1]	Cr 170 I**	I 167 Col$_h$**
ES12:TNF[4:1]	Cr 145 I**	I 140 Col$_h$**
ES12:TNF[9:1]	Cr 78 I**	I 68 Col$_h$**
ET13	Cr 39 (39.43) I*	No transition
ET13:TNF[1:2]	Cr 145 I**	I 135 Col$_h$**
ET13:TNF[1:1]	Cr 135 I**	I 126 Col$_h$**
ET13:TNF[2:1]	Cr 86 I**	I 77 Col$_h$**
ET13:TNF[4:1]	Cr 40 I**	No transition
ET14	Cr 36 (39.82) I *	No transition
ET14:TNF[1:1]	Cr 95 I**	I 88 Col$_h$**
ET14:TNF[2:1]	Cr 85 I**	I 75 Col$_h$**
ET14:TNF[4:1]	liquid	
ET27	Cr 37 (52.9) I*	No transition
ET44′	Cr 55 (47.2) I*	No transition

*From DSC and POM, ** From POM
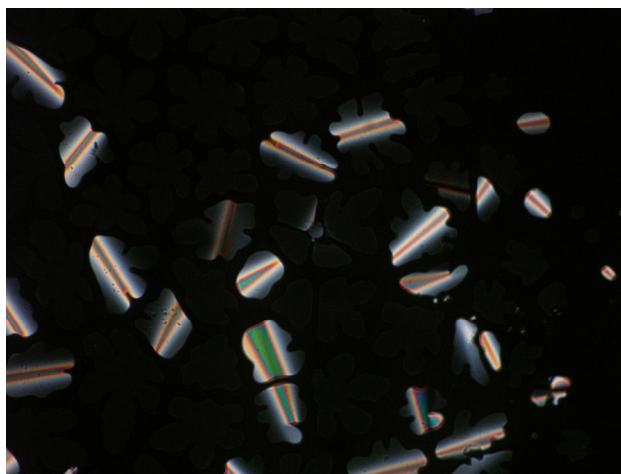
[a]
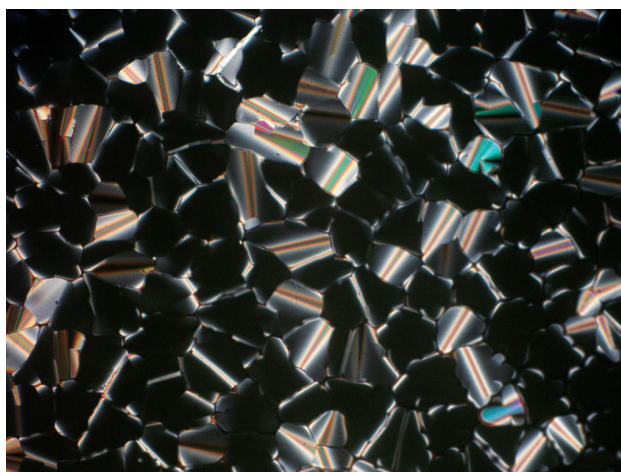
[b]

Figure 10: Optical textures for the mesophase of the doped dimer **ES12: TNF** in 1:1 ratio (a) cooling rate 2°C/min at 180°C (b) cooling rate 4°C/min at 170°C.
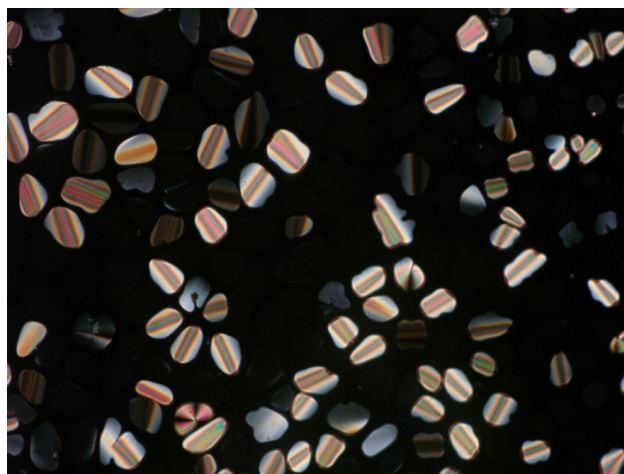
[a]
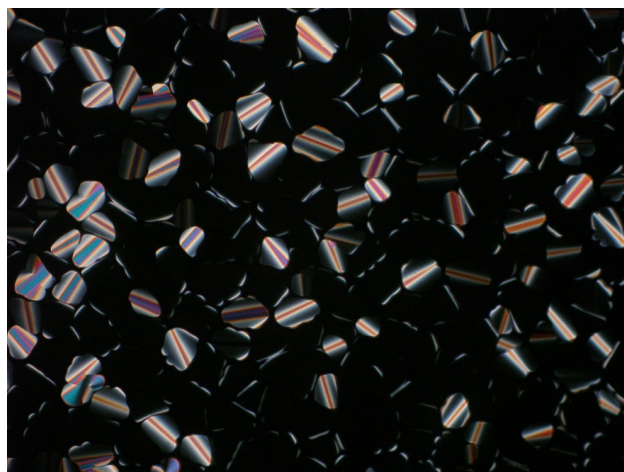
[b]

Figure 11: Optical textures for the mesophase of the doped dimer **ES12: TNF** in 2:1 ratio [a] cooling rate 2°C/min at 163°C and [b] cooling rate 4°C/min at 158°C.
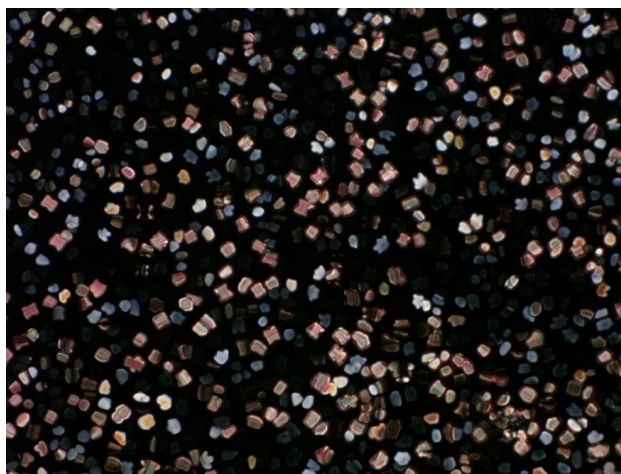
[a]

[b]

Figure 12: Optical textures for the mesophase of the doped dimer **ES12** in [a] 4:1 (dimer: TNF) ratio at 126°C and [b] 9:1 (dimer: TNF) ratio at 55°C.

[a]

[b]

Figure 13: Optical textures for the mesophase of the doped dimer **ET13** in [a] 1:1 (dimer: TNF) ratio at 89°C and [b] 2:1 (dimer: TNF) ratio at 50°C.

Figure 14: Optical textures for the mesophase of the doped dimer **ET14** in 1:1 (dimer: TNF) ratio at 70°C.

It would be interesting to compare the thermal behaviour of these *dimers* with the thermal behaviour of some reported *dimers* and trimers. Dipolar interaction of nitro group was found to be vital for liquid crystalline behavior in three fold symmetric benzene-bridged triphenylene trimers.[43] On the basis of *dimers* discussed here and trimers mentioned in the above reference, one can conclude that irrespective of the spacer length as well as linkage group, combination of central benzene core to two or more triphenylene units does not produce any mesomorphism unless these systems were functionalized or treated with a strong electron acceptor. If we compare the structure of these triphenylene-benzene-triphenylene *dimers* with that of triphenylene-triphenylene-triphenylene trimers[14c] and triphenylene-anthraquinone-triphenylene trimers,[44] it can be concluded that incorporation of all discotic mesogens in a single trimeric molecule results in mesomorphic behaviour. In present case, due to non-mesogenic central unit a mesogen-nonmesogen-mesogen system forms, which ultimately results in collapse of core-to-core interaction and hence these materials fail to exhibit liquid crystalline behavior. The presence of a metastable Col_h phase in methylene-bridged triphenylene-based unsymmetrical dimer having almost equal number of carbon atoms in spacer as well as periphery was reported by Hirst et. al.[27] Further, longer lived glassy Col_h was displayed by methylene-bridged triphenylene-based unsymmetrical dimer having

[43] S. Kumar, M. Manickam, *Liq. Cryst.*, 26, 939, **1999**.
[44] S. K. Gupta, V. A. Raghunathan, S. Kumar, *New J. Chem.,* 33, 112, **2009**.

different alkyl chains length around both cores. Thus the flexibility of the spacer allows the self-assembly of molecules in these systems.[14g]

2.9.2. X-ray diffraction studies of charge transfer complexes

In order to reveal the mesophase structure and hence the supramolecular organization of binary mixtures, X-ray diffraction experiments were carried out using unoriented samples. Diffraction patterns of the binary mixtures were recorded in their columnar phase while cooling from the isotropic phase. As a typical example, the diffraction pattern of **ET13**: TNF [1:1] and the intensity *vs.* theta (θ) profile derived from it are shown in Figure. 15. Qualitatively all the binary mixtures show similar diffraction patterns.
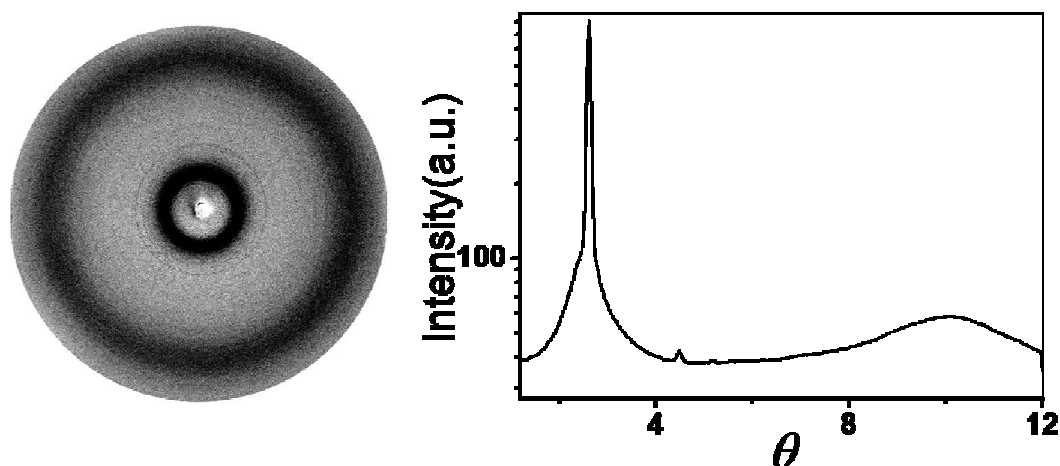
Figure 15: X-Ray diffraction pattern and intensity *vs.* θ profile of **ET13**: TNF [1:1] at 70°C.

As can be seen from the Figure, in the small angle region, two sharp peaks, one very strong and one weak, 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 a diffuse reflection appears at 4.4 Å. This corresponds to the liquid like order of the aliphatic chains. The intercolumnar distances, *a*, calculated by 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 **ET13**: TNF [1:1] was found to be 19.6 Å. This value is far less than 39.45 Å, which is the maximum separation between the

centers of two triphenylene discs of a dimer (as calculated from simple molecular modeling). This suggests that the triphenylene discs of different *dimers* are randomly stacked along the columns and that the rigid as well as the flexible parts of the spacers occupy the intervening space between the columns.

Table 6: X-Ray diffraction data (Å) of *dimers*-TNF composites derived from their diffraction patterns.

Compound : TNF [ratio]	*d*-Spacing (Å)	Intercolumnar distance(Å)
ET13 : TNF [1:1]	16.96	19.58
ET14 : TNF [1:1]	17.06	19.70
ES12 : TNF [4:1]	17.46	20.16
ES12 : TNF [9:1]	18.04	20.83
H6TP[45]	19.5	22.52

On comparing diffraction data of dimer-TNF composites with those of hexahexyloxytriphenylene (H6TP),[45] it is evident that the intercolumnar distance decreases on adding TNF. Further, for a given dimer, the lattice parameter decreases monotonically with increasing proportion of TNF (Table 6). This shrinking of the lattice can be attributed to the fact that sandwiching of the much smaller TNF molecule in between two triphenylene discs creates more space in the intervening region between the columns for the flexible alkyl chains and spacers. Thus, the X-ray diffraction patterns of the mesophase exhibited by all the samples belonging to both the series are supportive of a discotic hexagonal columnar arrangement.

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

2.9.3. Electrical conductivity study

The direct current (dc) conductivity of pure dimer **ET13** and dimer **ET13**: TNF composites were performed in indium tin oxide (ITO) coated glass sandwich cells (10 nm × 5 nm) with a separation of 5 µm. The current measurements were carried out using a Keithley pico ammeter (Model 480) along with a constant voltage source and a temperature controller. Figure 16 shows the dc conductivity values measured at different temperatures for pure dimer **ET13**, a 1:1 composite (50% TNF), and a 2:1 composite (66% TNF) of the dimer while cooling from isotropic temperature.
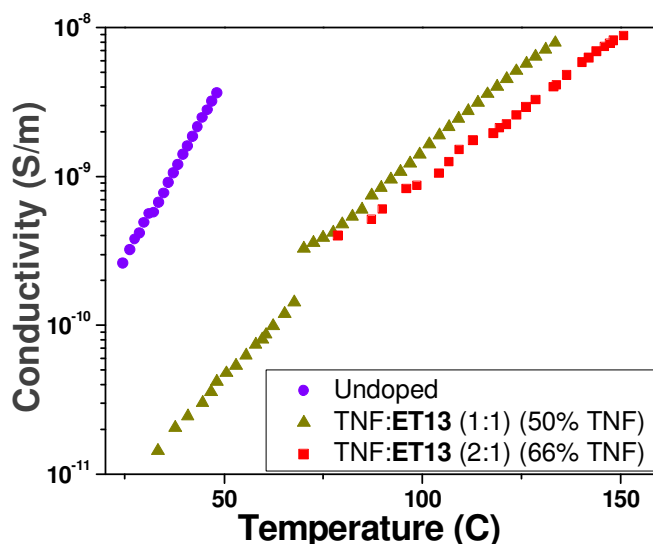
Figure 16: The variation of measured DC conductivity values as a function of temperature for 2:1, 1:1 ratio composite of dimer **ET13** with TNF and neat dimer **ET13**.

It can be seen that the measured conductivity values decrease while cooling. There is a sudden drop in the measured conductivity from about 3.29×10^{-10} to 1.44×10^{-10} S/m on cooling from 70.1 to 67.7 °C. Interestingly, these composites did not exhibit any first-order transition in DSC at different scan rates, during cooling either at this temperature range or closer to room temperature. Moreover, no textural change was observed in POM during the entire range of cooling. However, the mobility of the mesophase at room temperature was very low. Probably, the sample vitrifies at a certain temperature while cooling. It is of significance that the electrical conductivity measurements exhibit a significant drop in value at

this temperature signifying a decrease in the charge mobility. In other words, the decrease in the conductivity at lower temperatures could be attributed to a phase transition from a columnar mesophase to a vitrified state. A similar trend was observed for a 2:1 composite (66% TNF) of TNF with dimer **ET13**. We were unable to observe any regular trend in conductivity below 78.7 °C in this case due to intense fluctuation in conductivity values. The decrease in charge mobility in the glassy phase of triphenylene-based discotic *dimers* is well-documented in the literature.[14b]

The dc conductivity values measured in these systems are however, very much lower than that observed previously for monomeric triphenylene systems doped with various electron acceptors.[46-52] Smaller values of conductivity can be linked to a short-range order of discs within an individual column. In the case of monomeric triphenylene systems, discs are free to stack one upon the other to construct a compact column. One of the essential conditions for charge mobility in the columnar discotic phase is the long-range defect-free mesophase that can be realized only when the discs are packed closely. Therefore, we attribute the lower conductivity values in the dimer as well as its composites as due to the long methylene spacer and benzene ring acting as diluents which reduces the ability of triphenylene discs and flat TNF molecules to pack closely within the column, resulting in reduced π-π overlap over its entire length.

There are several reports in the literature on the dc conductivity studies in discotic columnar liquid crystal medium. Most of these studies relate to the effect of doping different electron acceptors as well as donors on the electrical conductivity. A large increase in the conductivity has been observed after doping with iodine,[46] TNF,[47,48] gold nanoparticles,[49,50] triphenylene-capped gold nanoparticles,[51] and ferrocenium ions.[52] The increase in the electrical conductivity in these systems arises from the charge transfer complex formation

[46] G. B. Vaughan, M. P. A. Heiney, J. P. McCauley Jr., A. B. Smith III, *Phys Rev B,* 46, 5, 2787, **1992**.
[47] S. Chandrashekhar, V. S. K. Balagurusamy, *Proc. R. Soc. Lond. A,* 458, 1783, **2002**.
[48] V. S. K. Balagurusamy, S. K. Prasad, S. Chandrashekhar, S. Kumar, M. Manikam, C. V. Yalamaggad, *Pramana*, 53, 1, 3, **1999**.
[49] S. Kumar, V. Lakshminarayanan, *Chem. Commun.,* 1600, **2004**.
[50] S. Kumar, S. K. Pal, V. Lakshminarayanan, *Mol. Cryst. Liq. Cryst.,* 434, 251, **2005**.
[51] S. Kumar, S. K. Pal, P. S. Kumar, V. Lakshminarayanan, *Soft Matter,* 3, 896, **2007**.
[52] P. S. Kumar, S. Kumar, V. Lakshminarayanan, *J. Phys. Chem. B,* 112, 4865, **2008**.

with the triphenylene core acting as donor and the dopants acting as acceptors. On the application of the electric field, due to an increase in charge migration, the electrical conductivity rises, which can be explained by the hopping formalism.

Figure 16 also shows the dc conductivity values measured at different temperatures for the nonliquid crystalline pure dimer **ET13**. It can be seen that for this system, the dc conductivity values increase from 2.61×10^{-10} to about 3.63×10^{-9} S/m in the temperature range of 24.5-48.2 °C. It was earlier observed in the case of the undoped monomeric hexaheptyloxytriphenylene system that the electrical conductivity values are measured to be of the order of 10^{-10} S/m in the columnar hexagonal phase which increases to about 5×10^{-9} in the isotropic phase at higher temperature.[51] The dimer **ET13** did not show any sign of crystallization or mesophase formation on cooling from the isotropic phase. We performed X-ray diffraction experiments for the dimer **ET13** at room temperature while cooling from the liquid phase (Figure 17). The presence of a broad peak rules out the existence of any ordered liquid crystal or crystal phase after cooling from isotropic temperature. The observation of small, but considerable dc conductivity in these cases in the isotropic phases is surprising, but can be explained by significant charge carrier mobility at these temperatures. Power *et al.*[53] measured the DC conductivity of pure alcohols, 5-methyl-2-hexanol and 1-propanol. The conductivity observed for these alcohols (2.4-5.0×10^{-10} S/m) is comparable to our discotic materials indicating the highly disordered nature of both systems.

[53] G. Power, J. K. Vij, G. P. Johari, *J. Phys. Chem. B*, 111, 11201, **2007**.
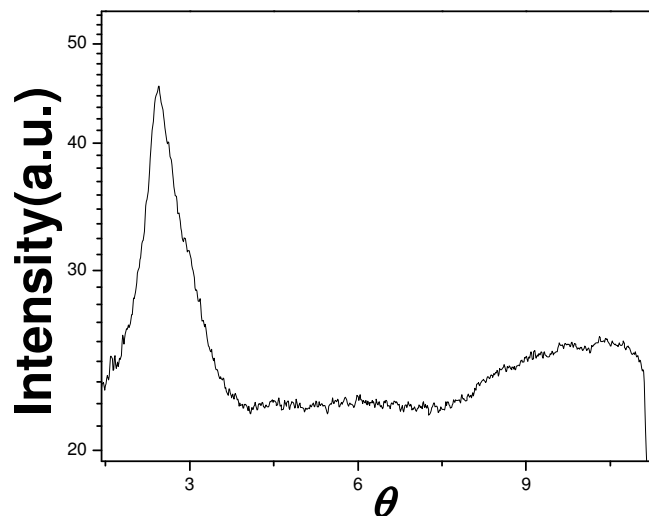
Figure 17: Intensity *vs.* θ profile of **ET13** at room temperature while cooling.

We also find that conductivity values for the nonliquid crystalline pure dimer **ET13** are comparable to the value observed for the dimer-TNF composite at the liquid crystalline phase at higher temperatures. In the case of the dimer-TNF composite, though the charge transfer interaction is good enough for stacking of molecules into columns and hence the induction of mesomorphic behavior, the dilution of an individual column caused by a methylene spacer and benzene ring plays a predominant role in reducing the π-π overlap for the entire column length. Therefore the dc conductivity value of about 2.16×10^{-9} S/m at 106.7 °C observed for the liquid crystalline phase of 50% dimer:TNF composite is nearly 7 orders of magnitude lower than that of monomeric hexahexylthiotriphenylene (HHTP) when doped with 0.62 mol % TNF, acting as an electron acceptor.[48] The large disparity of electrical conductivity values for the TNF doped liquid crystalline states in these two systems can be understood by the reduced overlap of the discs in the dimer **ET13** compound due to the long methylene spacer and benzene ring bridging the triphenylene cores disrupting the stacking, as discussed earlier.

2.9.4. Scanning Tunneling Microscopy (STM) Imaging

Discotic liquid crystals, being supramolecules, lend themselves for clear imaging in STM. There are several reports of the STM of triphenylene-based discotic liquid crystals in

the literature.[54] In this work, the STM studies were carried out using Pico plus (molecular imaging) SPM. The images shown here are plane-corrected using a scanning probe image processor (SPIP) software (Image Metrology, Denmark) and filtered to remove noise. The sample was dissolved in dichloromethane, and a drop of it is spread on a highly oriented pyrolytic graphite surface and allowed to evaporate. The images were obtained using cut tungsten tip at a constant height mode of scanning with a sample bias of +100 mV.
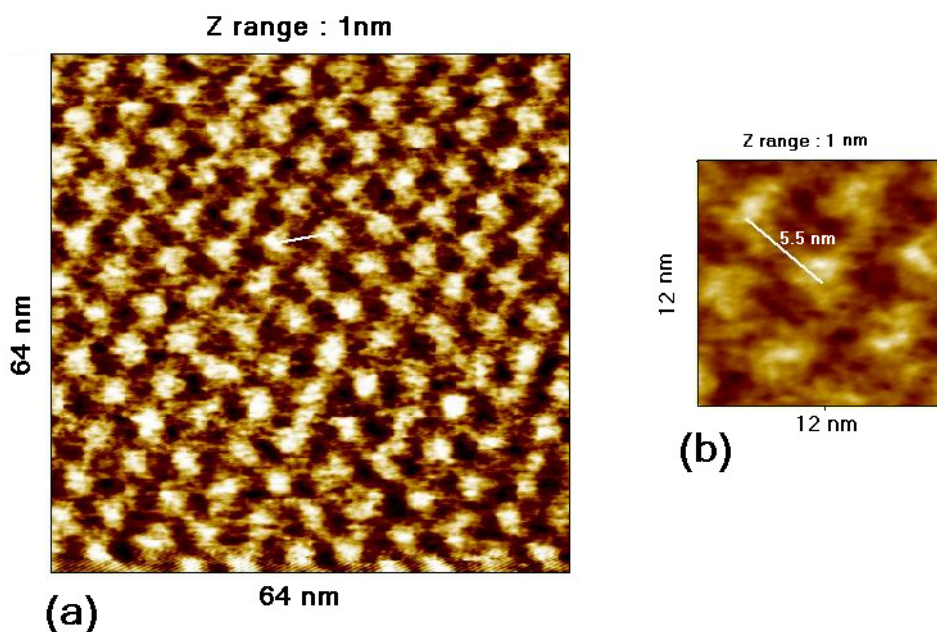

Figure 18. (a) STM image of the triphenylene-benzene dimer **ET13** on HOPG surface. **(b)** A zoomed portion of the image showing the hexagonal lattice. The bright spots correspond to triphenylene core and the distance marked in (b) corresponds to 5.5 nm.

The STM image of **ET13** (Figure 18) shows clearly resolved bright spots which are organized in two-dimensional hexagonal lattice with a center-center distance of 5.5 nm. The diameter of the molecule is about 6.5 nm including the alkyl chains. The image shows that the molecules are lying flat on the surface with the triphenylene-benzene dimer **ET13** rings lying in a face-on orientation over the graphite surface essentially forming a monolayer sheet. This orientation is driven by the π-π interaction between the aromatic core of a triphenylene

[54] (a) X. J. Ma, Y. L. Yang, K. Deng, Q. D. Zeng, C. Wang, K. Q. Zhao, P. Hu, B. Q. Wang, *ChemPhysChem*, 8, 2615, **2007**; (b) S. D. Ha, Q. Zhang, S. Barlow, S. R. Marder, A. Kahn, *Phys. Rev. B*, 77, 085433, **2008**; (c) S. Xu, Q. Zeng, J. Lu, C. Wang, L. Wan, C. L. Bai, *Surf. Sci.*, 538, L451, **2003**; (d) N. Katsonis, A. Marchenko, D. Fichou, *Synth. Met.*, 147, 73, **2004**.

molecule and the graphite surface. Since the distance of 5.5 nm between the two triphenylene dimer cores is less than their diameter by 1 nm, the alkyl chains are not lying flat on the graphite surface presumably due to the higher van der Waals interaction between the alkyl chains of the adjacent molecules. The intercalated alkyl chains of neighboring molecules are assumed to be projecting out of the graphitic plane.

2.10. Conclusion

We have synthesized two series of symmetrical disk-rod *dimers* composed of two triphenylene units linked *via* a spacer having both rigid and flexible parts in it. In addition to this, we have changed the relative orientation of two disk moieties with respect to each other. These *dimers* were not liquid crystalline, but when doped with TNF, each gave a hexagonal columnar phase with distinct optical texture, which was further confirmed by X-ray diffraction. Due to incorporation of rigid portion, the flexibility of methylene spacer gets disturbed because of benzene ring and finally stacking of triphenylene cores become difficult. On doping with TNF, core to core interaction of triphenylene rings becomes more important as a consequence of charge transfer interaction and thus, these complexes form hexagonal columnar mesophase, which vitrifies at low temperature. The phase transition from the liquid crystalline state to a glassy state is clearly indicated by a sudden drop in dc electrical conductivity.

2.11. Experimental

2.11.1. General information

Chemicals and solvents (AR quality) were used without any purification. All reactions were monitored by employing TLC technique using appropriate solvent system for development. Degassed solvents were used in the reaction involving oxygen sensitive materials. Transfer of moisture sensitive materials were carried out under N_2 atmosphere using standard syringe-septum techniques. All solvent extracts were washed successively with water, brine, and dried over anhydrous sodium sulphate and concentrated at reduced pressure on a Buchi rotary evaporator. Yields reported are isolated yields of pure materials. The purity

of all the compounds was confirmed from their homogeneous nature of a TLC plate, NMR spectrum and elemental analyses.

2.11.1.1.   Column chromatography

Chromatographic separations were performed on silica gel (100-200 mesh, ACME) or over silica gel (230-400 mesh, ACME).

2.11.1.2.   Thin-layer chromatography

Thin-layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck, Kieselgel 60, F254). Visualization of the spots on TLC plates was achieved by exposure to UV light.

2.11.1.3.   Transition temperatures

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, 10 and 20 ºC min^{-1}. The apparatus was calibrated using indium (156.6 ºC) as a standard. Textural observation of the mesophase was carried out using polarizing optical microscopy (Olympus BX51) provided with a heating stage (Mettler FP82HT) and a central processor (Mettler FP 90).

2.11.1.4.   X-ray diffraction studies

X-ray diffraction (XRD) was carried out in powder samples using using Cu-K$_\alpha$ (λ = 1.54 Å) radiation from a Rigaku ultrax 18 rotating anode generator (4 kW) monochromated with a graphite crystal. The samples were held in sealed Lindemann capillary tubes (0.7 mm diameter) and the diffraction pattern were collected on a two-dimensional Marresearch image plate. A magnetic field of about 5 k Gauss was used to align the samples, however a perfect alignment of the mesophase could not be achieved.

2.11.1.5. Ultraviolet spectra

Ultraviolet spectra recorded on UV-Visible Spectrophotometer (Hitachi U-3200).

2.11.1.6. IR spectra

IR spectra were recorded on Shimadzu FTIR-8400 spectrophotometer. IR spectra were obtained in Nujol mull and in KBr discs.

2.11.1.7. ^{1}H NMR & ^{13}C NMR

^{1}H NMR and ^{13}C NMR were recorded on a Brucker AMX 400 spectrometer at Indian Institute of Science. All chemical shifts were recorded in ppm units downfield from Me_4Si, and J values are given in Hz.

2.11.1.8. Elemental analysis

Elemental analyses were performed on a Carlo-Erba 1106 analyser.

2.11.2. Synthesis

2.11.2.1. General procedure for the synthesis of Monohydroxypentaalkoxytriphenylene 35

A solution of hexahexyloxy triphenylene **34** (3 gm, 3.6 mmol) in dry dichloromethane was stirred at 0 C for 20 minutes under nitrogen atmosphere. To the above solution was then added B-bromocatecholborane (0.86 gm, 4.3 mmol). The resultant solution was then stirred at room temperature for 48 hours under nitrogen atmosphere. The excess of dichloromethane was evaporated from the reaction mixture. The residue was passed through a neutral alumina column to isolate the pure product **35** from unwanted side products and unreacted starting material in about 40 % yield.

2.11.2.2. General procedure for the synthesis of hydroxyl-functionalized triphenylene 36

To a warm solution of monohydroxy triphenylene **35** (1 eq) and potassium carbonate (4 eq) in ethyl methyl ketone was added 6-bromohexanol-1 (1.2 eq). The resultant solution was then refluxed for about 12 hours. The reaction mixture was filtered after completion of reaction (TLC indication). The filtrate was concentrated in vacuum and the residue was passed through a silica gel column (eluant: 20% ethyl acetate in hexane). Finally, the material was recrystallized from hexane to furnish the desired intermediate **36** in about 79 % yield.

2.11.2.3. Synthesis of ES14

To a solution of terphthalic acid **37** (26.6 mg, 0.16 mmol), hydroxyl-functionalized triphenylene **36** (287 mg, 0.34 mmol) and N,N′-dicyclohexylcarbodiimide (DCC) (78.3 mg, 0.38 mmol) in dry dichloromethane, was added catalytic amount of 4-dimethylaminopyridine (DMAP). The reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction solvent was evaporated and the crude product was purified by silica gel chromatography (eluant: 10% ethyl acetate in hexane). The final product was achieved by recrystallization from hexane. Yields, 65 %.

ES14

^{1}H NMR: (400 MHz, CDCl$_3$): δ 8.08 (s, 4H), 7.83 (s, 12H), 4.37 (t, J = 6.6 Hz, 4H), 4.23 (t, J = 5.9 Hz, 24H), 1.93 (m, 20H), 1.85 (m, 4H), 1.67 (m, 4H), 0.8-1.6 (m, 98H). ^{13}**C NMR:** (100 MHz, CDCl$_3$): δ 234.2, 231.6, 206.6, 153.2, 115.5, 77.3, 77.0, 76.7, 68.4, 33.7, 32.7, 29.2, 27.9, 25.3.

Elemental analysis: Calcd for C$_{116}$H$_{170}$O$_{16,}$ C 76.53, H 9.41; Found C 76.22, H 9.56 %.

2.11.2.4.   Synthesis of ES13

To a solution of isophthalic acid **38** (26.6 mg, 0.16 mmol), hydroxyl-functionalized triphenylene **36** (287 mg, 0.34 mmol) and DCC (78.3 mg, 0.38 mmol) in dry dichloromethane, was added catalytic amount of DMAP. The reaction mixture was stirred at room temperature for 48 hours. After the completion of reaction solvent was evaporated and the crude product was purified by silica gel chromatography (eluant: 10% ethyl acetate in hexane). The final product was achieved by recrystallization from hexane. Yields, 62 %.

ES13

^{1}H NMR: (400 MHz, CDCl$_3$): δ 8.7 (s, 1H), 8.2 (dd, J = 7.8 and 1.6 Hz, 2H), 7.82 (s, 12H), 7.47 (t, J = 7.8 Hz, 1H), 4.37 (t, J = 6.6 Hz, 4H), 4.22 (t, J = 5.9 Hz, 24H), 1.94 (m, 20H), 1.85 (m, 4H), 1.67 (m, 4H), 0.8-1.6 (m, 98H).

Elemental analysis: Calcd for C$_{116}$H$_{170}$O$_{16,}$ C 76.53, H 9.41; Found C 76.56, H 9.15 %.

2.11.2.5.   Synthesis of ES12

Compound **ES12** was prepared as described above in 68% yield.

ES12

^{1}H NMR: (400 MHz, CDCl$_3$): δ 7.81 (s, 12H), 7.68 (q, J = 3.3 Hz, 2H), 7.48 (q, J = 3.3 Hz, 2H), 4.34 (t, J = 6.6 Hz, 4H), 4.22 (t, J = 5.9 Hz, 24H), 1.93 (m, 20H), 1.81 (m, 4H), 0.8-1.75 (m, 102H).

Elemental analysis: Calcd for C$_{116}$H$_{170}$O$_{16,}$ C 76.53, H 9.41; Found C 76.10, H 9.68 %.

2.11.2.6.   General procedure for the synthesis of *ω*-bromo-substituted triphenylene 40

In a typical reaction, a mixture of monohydroxy pentaalkoxy triphenylene **35** (1 eq), dibromohexane (7 eq) and caesium carbonate (8 eq) in ethyl methyl ketone was refluxed for

overnight. After completion of reaction (TLC indication) the reaction mixture was cooled, filtered. The filtrate was concentrated by evaporating solvent to dryness under reduced pressure. The residue was purified by silica gel chromatography (eluant: 10 % ethyl acetate in hexane). Solvent was then removed in rotatory evaporator. The residue left was now dissolved in dichloromethane and the resulting solution was added to cold methanol to afford the desired intermediate **40** in about 66 % yield.

2.11.2.7.   Synthesis of ET13

A mixture of compound **40** (297.7 mg, 0.30 mmol), resorcinol **41** (9.5 mg, 0.086 mmol) and Cs_2CO_3 (281.5mg, 0.864 mmol) was dissolved in N-Methylpyrrolidone (NMP). The mixture 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 6 times till the reaction completes (TLC monitoring). It was then poured into excess of distilled water and then extracted with chloroform. The combined organic layer was washed with distilled water and water layer was washed with ethyl acetate. Both organic layers were mixed, dried over anhydrous sodium sulphate and evaporated to dryness under reduced pressure. The residue was purified by silica gel chromatography (eluant: 5 % ethyl acetate in hexane). Solvent was then removed in rotatory evaporator. The residue left was now dissolved in dichloromethane and the resulting solution was added to cold methanol to afford **ET13,** Yield 78 %.

ET13

^{1}H NMR: (400 MHz, CDCl$_3$): δ 7.83 (s, 12H), 7.14 (t, *J* = 8 Hz, 1H), 6.48 (s,1H), 6.46 (unresolved, 2H), 4.23 (t, *J* = 6.5 Hz, 24H), 3.91 (t, *J* = 6.5 Hz, 4H), 1.94 (m, 24H), 1.76 (m, 4H), 0.8-1.7 (m, 122H).

Elemental analysis: Calcd for $C_{126}H_{194}O_{14,}$ C 78.3, H 10.1; Found C 77.9, H 9.96%.

2.11.2.8.   Synthesis of ET14

Hydroquinone **42**, was used in place of resorcinol to synthesize **ET14.** Synthetic methods were similar to the manner described above for **ET13.**

ET14

¹H NMR: (400 MHz, CDCl₃): δ 7.83 (s, 12H), 6.8 (s, 4H), 4.23 (t, J = 6.5 Hz, 24H), 3.88 (t, J = 6.6 Hz, 4H), 1.94 (m, 24H), 1.74 (m, 4H), 0.8-1.7 (m, 122H).

2.11.2.9.   Synthesis of ET27

2, 7-dihydroxynephthalene **43**, was used in place of resorcinol to synthesize **ET27.** Synthetic methods were similar to the manner described above for **ET13.**

ET27

¹H NMR: (400 MHz, CDCl₃): δ 7.83 (s, 12H), 7.63 (d, J = 8.8 Hz, 2H), 7.01 (d, J = 2.4 Hz, 2H), 6.98 (dd, J = 8.8 Hz, 2H), 4.23 (t, J = 6.5 Hz, 24H), 4.04 (t, J = 6.5 Hz, 4H), 1.94 (m, 24H), 1.83 (m, 4H), 0.8-1.7 (m, 122H).

2.11.2.10.   Synthesis of ET44'

4, 4'-dihydroxybiphenyle **44** was used in place of resorcinol to synthesize **ET44'.** Synthetic methods were similar to the manner described above for **ET13.**

ET44'

¹H NMR: (400 MHz, CDCl₃): δ 7.83 (s, 12H), 7.43 (d, J = 8.6 Hz, 2H), 6.93 (d, J = 8.8 Hz, 2H), 4.23 (t, J = 6.5 Hz, 24H), 3.96 (t, J = 6.5 Hz, 4H), 1.94 (m, 24H), 1.78 (m, 4H), 0.8-1.7 (m, 122H).