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To cite this article: Budur N. Alanazi, Anoud M. Alruwaili, Rhoda D. Beskeni, Andrew N. Cammidge & Saeed S. Samman (2021): Pentaalkoxytriphenylene monoesters and their dyads; structural factors influencing columnar and nematic mesophase behaviour, *Liquid Crystals*, DOI: [10.1080/02678292.2021.1993456](https://doi.org/10.1080/02678292.2021.1993456)

To link to this article: <https://doi.org/10.1080/02678292.2021.1993456>



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Published online: 08 Nov 2021.



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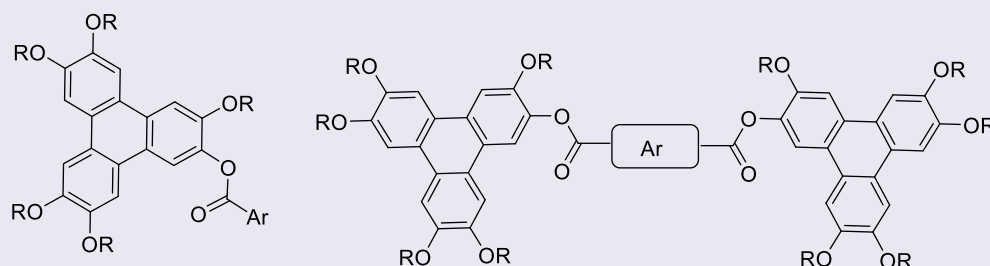
Pentaalkoxytriphenylene monoesters and their dyads; structural factors influencing columnar and nematic mesophase behaviour

Budur N. Alanazi, Anoud M. Alruwaili, Rhoda D. Beskeni, Andrew N. Cammidge and Saeed S. Samman

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ABSTRACT

Ester linkages are frequently employed in the design of discotic liquid crystals, and indeed the first examples of discotic liquid crystals reported by Chandrasekhar, Sadashiva and Suresh were hexaesters of benzene. Within the wide range of liquid crystalline triphenylene systems so far reported, the symmetrical hexa(aryl) esters are particularly noteworthy because they form the relatively rare and technologically important discotic nematic mesophase. An alternative strategy for inducing nematogenic behaviour is to build linked and twinned structures, and here we report examples of materials that combine the two design features. Pentaalkoxy triphenylenes bearing a single aryl ester retain the columnar mesophase. Linked dyad structures promote nematic phase formation and stability is influenced by the link type and bonding arrangement within isomeric series (phthalates) and related constructs.



Mesophase behaviour of monomeric triphenylene esters and related dyad structures

ARTICLE HISTORY

Received 13 July 2021
Accepted 11 October 2021

KEYWORDS

B. K. Sadashiva;
triphenylenes; discotics;
synthesis; nematic

Introduction

The first examples of discotic liquid crystals reported by Chandrasekhar, Sadashiva and Suresh were hexaesters of benzene (1) [1] and ester linkages are common in liquid crystal science. Triphenylene based liquid crystals were reported soon after the initial report [2,3] and the triphenylene nucleus has become the most widely studied and versatile core [4–6] in discotic systems [7]. Within the symmetrical, hexasubstituted series, the heavily studied hexaethers (2) form stable columnar mesophases [4,5], while hexa(aryl) esters (3) form the much rarer discotic nematic phase [8–10]. New synthetic chemistry has given relatively straightforward access to complex, often unsymmetrical derivatives, for both applications and to probe liquid crystal behaviour. Our group has made a number of contributions to this

area and we find that breaking the symmetry can have a significant effect on mesophase stability and range. The overall observation, however, is that columnar mesophase formation dominates in monomeric systems [11–15], and in systems linked by flexible spacers of appropriate length [16–18]. More recently we have turned our attention to exploring structural features that support discotic nematic mesophase formation. We and others have found that nematic mesophase formation becomes favourable when triphenylene mesogens are linked via rigid spacers to form dyads (5) (single link point) [19] or rigid twins (e.g. 6, 7) (two link points to give a macrocycle) [20–22]. Selected examples are shown in Figure 1. Here we report the initial results of combining the two known features for inducing nematic behaviour – triphenylene esters and dyad formation.

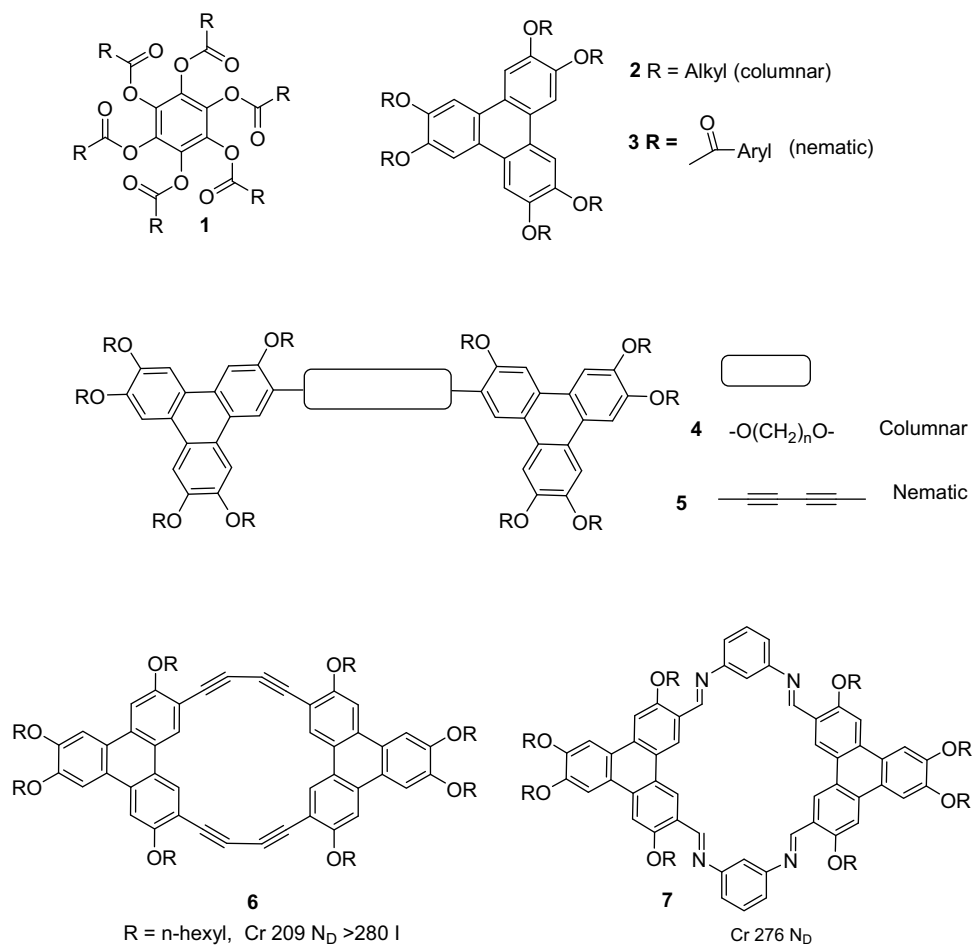
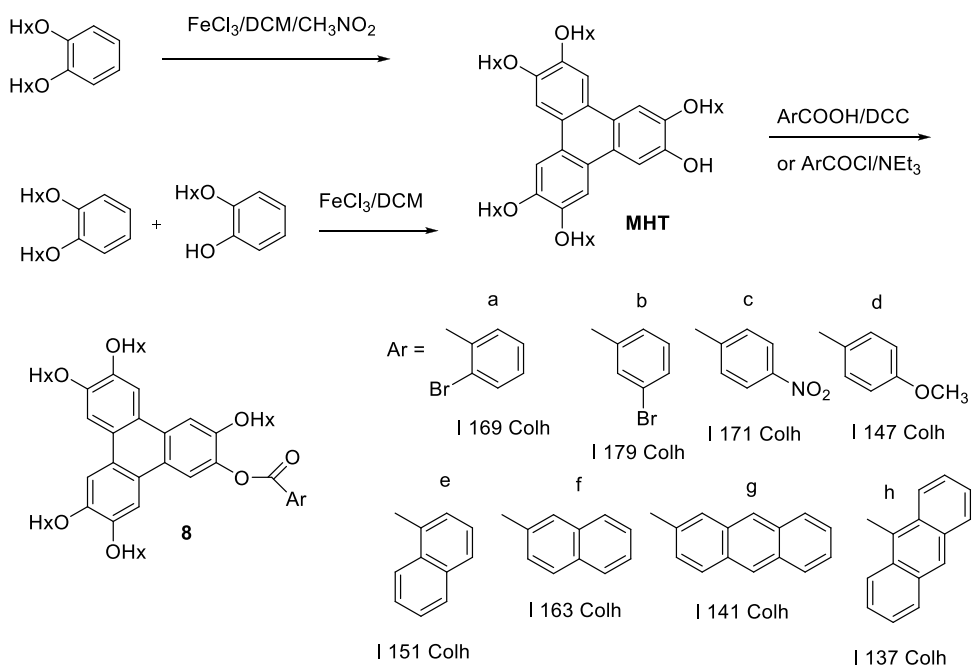


Figure 1. Examples of discotic liquid crystals, including dyads and twins.



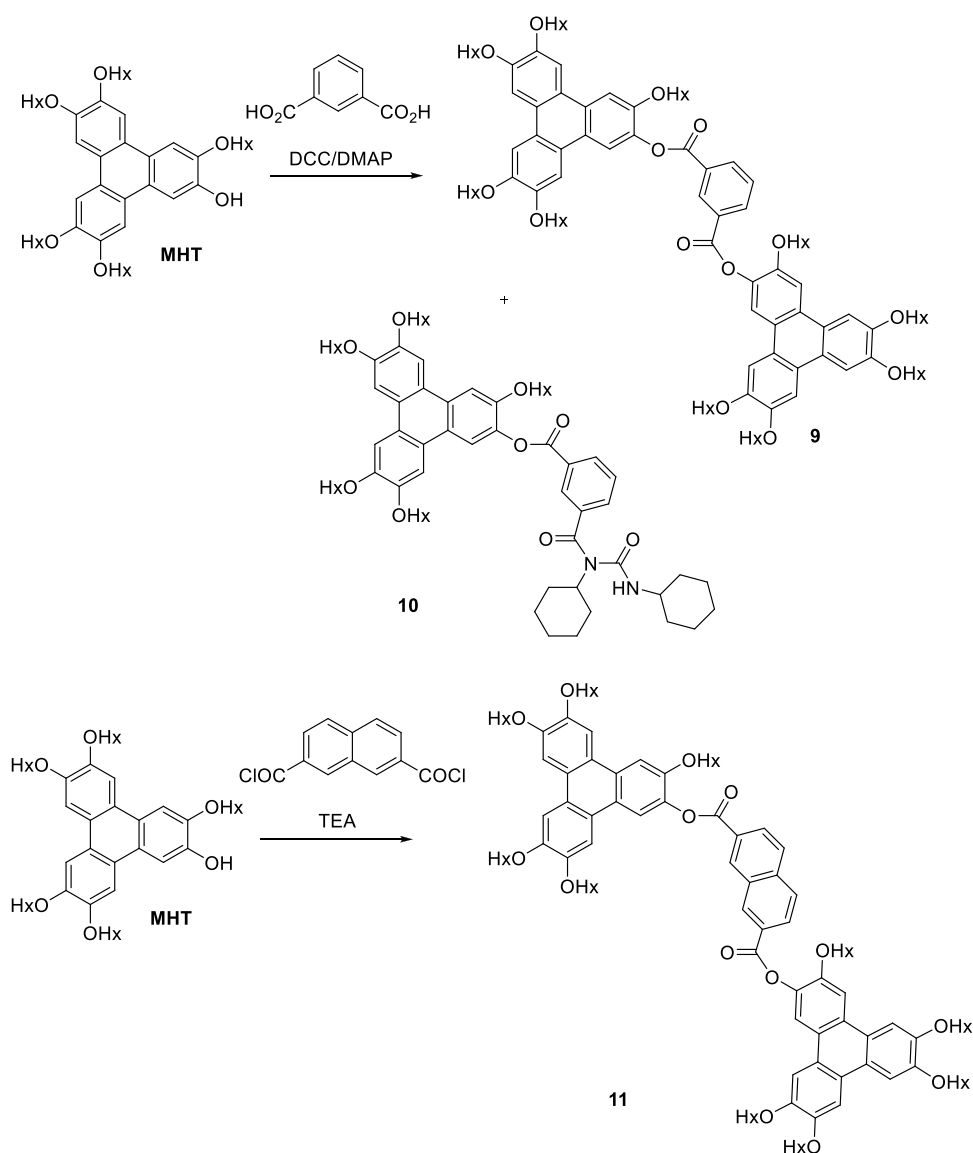
Scheme 1. Synthesis, structures and mesophase behaviour of penta(hexyloxy)triphenylene monoesters **8** (Hx = n-hexyl).

Discussion

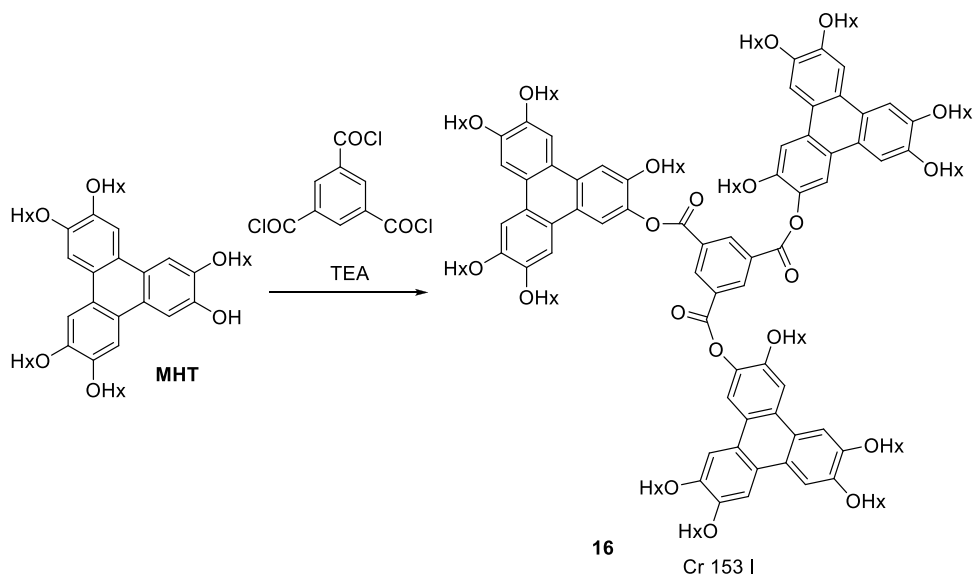
Triphenylene monoesters

The starting material for all monoester syntheses was 2-hydroxy-3,6,7,10,11-pentakis(hexyloxy) triphenylene (MHT – ‘monohydroxytriphenylene’). It was prepared by two known routes, either directly from dihexyloxybenzene (oxidative trimerisation followed by hydrolysis under the reaction conditions) [23] or by oxidative trimerisation of a mixture of dihexyloxybenzene and hexyloxyphenol [24,25]. MHT was isolated by column chromatography and used immediately in ester synthesis. Ester formation was achieved by direct reaction of MHT with an excess of either the appropriate acid chloride, or by coupling with the partner carboxylic acid using DCC (Scheme 1).

The mesophase behaviour of the triphenylene mono(aryl) esters is also shown in Scheme 1. It is immediately apparent that the structure of the single aryl-ester has only a small effect on the mesophase stability of the materials. In most cases the unsymmetrical materials were isolated pure as precipitates that cleared to isotropic liquids at $\sim 150^\circ\text{C}$ – significantly higher than the symmetrical hexa(hexyloxy) triphenylene HAT6 ($\sim 100^\circ\text{C}$). Columnar hexagonal mesophases (assigned based on the characteristic textures) are observed on cooling. Introduction of a single ester group therefore does not on its own lead to the onset of nematic behaviour, but it does prevent crystallisation in the examples investigated and the columnar phase persists down to room temperature as a glass.



Scheme 2. The synthesis of triphenylene ester dyads and an example of the unwanted side products produced during DCC coupling (Hx = *n*-hexyl).



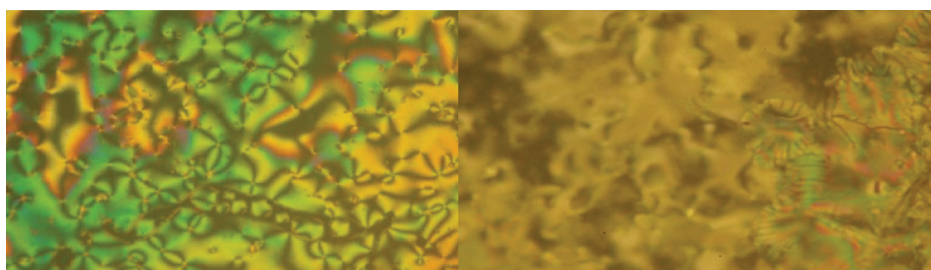
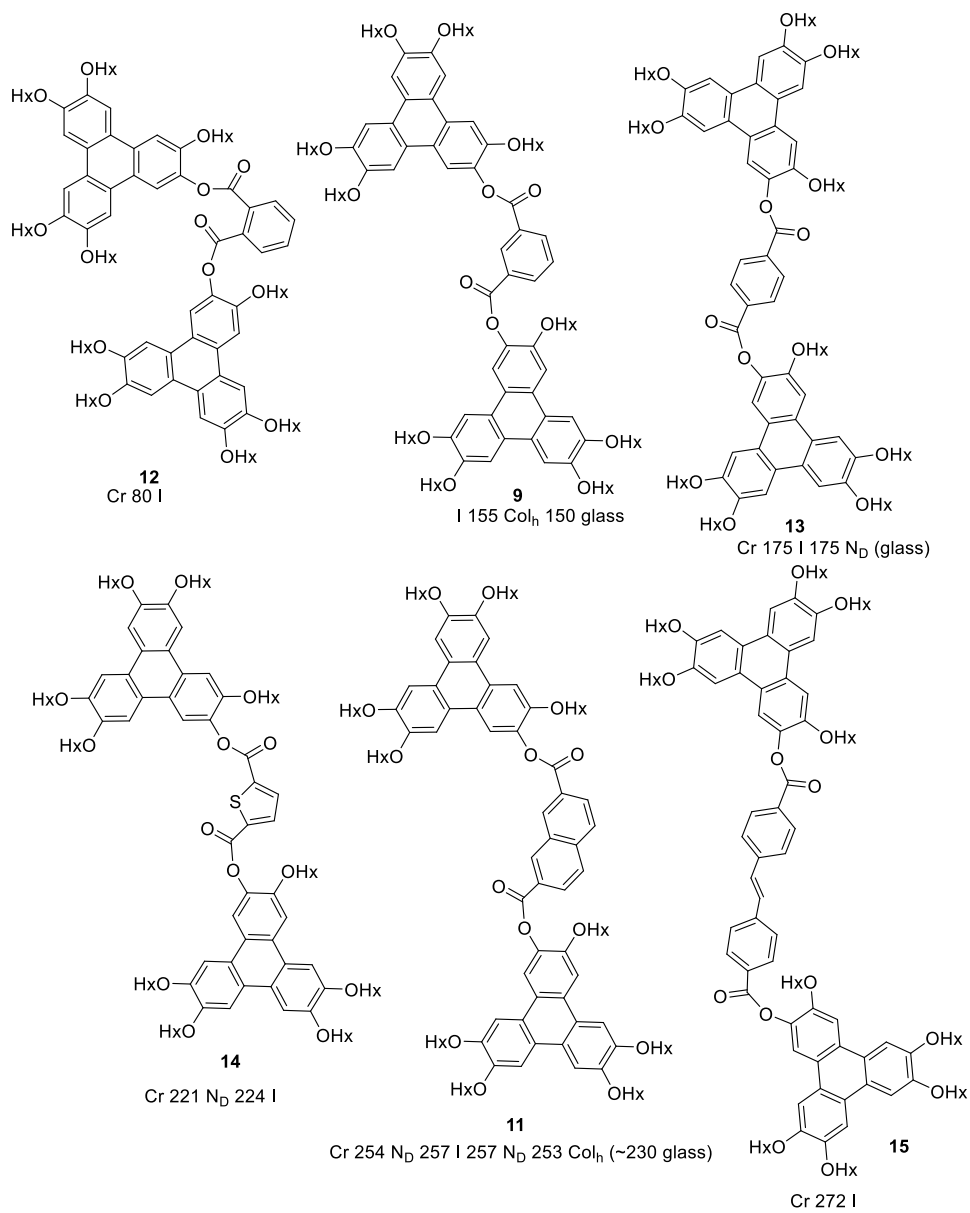
Scheme 3. The synthesis of triphenylene ester triad **16** (Hx = *n*-hexyl).

Triphenylene ester dyads and a triad

Triphenylene diesters linked by aryl dicarboxylates were selected because the joining unit has rigidity and geometry (conformation) constraints that lie between the fully flexible alkyloxy spacers (columnar) and the linear, rigid di-alkyne bridges (nematic). The isomeric phthalic acid series was selected, with the 1,2-, 1,3- and 1,4-arrangements each providing unique triphenylene-triphenylene preferred orientation. The syntheses of these twinned structures via the DCC coupling route proved more challenging than the corresponding simple monoesters. In the former case, employment of excess carboxylic acid (or acid chloride) allowed efficient conversion and isolation of the ester product. For dyad structures it was not practical to employ a large excess of MHT and reactions were complicated by the formation of side-products containing a single triphenylene and urea fragment originating from DCC (illustrated for one representative synthesis in [Scheme 2](#)). Separation by column chromatography was challenging but pure samples were eventually obtained for the three isomers. Two further examples were initially selected. Thiophene-2,5-dicarboxylic acid was coupled with MHT using DCC. The reaction was again complicated by competitive urea formation, but pure dyad was obtained after chromatography. The diester from naphthalene-2,7-dicarboxylic acid was most conveniently prepared via its acid chloride (prepared by treatment of the diacid with oxalyl chloride) ([Scheme 2](#)).

The thermal behaviour of the dyad structures was also investigated by polarising optical microscopy and is summarised in [Figure 2](#). Unsurprisingly,

triphenylene dyad **12** linked by the benzene 1,2-positions did not show any mesophase behaviour. It has a low (80°C) melting point, no doubt reflecting the difficulty such a bent molecular system has in achieving efficient packing that maximises intermolecular interactions, in either a crystal or liquid crystal phase. Isophthalate (1,3-) **9** and terephthalate (1,4-) **13** dyads have similar melting points. Isophthalate dyad **9** is isolated as an amorphous solid that clears fully at 155°C and reforms a columnar hexagonal phase on cooling (based on its characteristic fan texture) which forms a glass almost immediately (150°C). Linear terephthalate diester **13** melts directly to the isotropic liquid at 175°C. On cooling, regions of nematic and isotropic glass form simultaneously. It is noteworthy that a derivative, differing only by addition of a single vinyl substituent on the phthalate, has been reported to show stable columnar and nematic phases, perhaps emphasising the importance of symmetry-breaking in the systems to disfavour crystallisation [24]. For one sample the material was subsequently removed from the slide and re-examined by ¹H NMR spectroscopy which showed no evidence of decomposition during the heating cycle. The separation between triphenylene components was increased (in a linear manner) by linking through a stilbene (diester **15**). Stilbene ester **15** melts directly to an isotropic liquid at 272°C. Bent dyads linked by 2,5-thiophene **14** and 2,7-naphthalene **11** each displayed narrow range enantiotropic nematic mesophases while the latter also showed monotropic columnar hexagonal phase formation before forming a glass. Finally, triad **16** was

Dyad **14** at 222 °CDyad **11** at 253 °C
(monotropic Col_h growing from N_D)**Figure 2.** (Colour online) Structures and mesophase behaviour of triphenylene ester dyads (Hx = *n*-hexyl).

synthesised by reaction of MHT with the acid chloride derived from benzene-1,3,5-tricarboxylic acid. The triad shows no mesophase behaviour, and melts directly to isotropic liquid at 153°C.

Experimental

(2-Bromobenzoate) ester **8a**

MHT (150 mg, 0.0002 mol), 2-bromo benzoyl chloride (0.052 g, 0.00024 mol, 1.2 eq) and NEt₃ (1 ml) were stirred in CH₂Cl₂ (25 ml) at 0°C for 2 h. Methanol was added and the crude solid was collected by filtration and reprecipitated from DCM-methanol to give ester **8a** as an off-white solid (0.03 g, 16.6%). IR (thin film, cm⁻¹) 3534, 2972, 2855, 1746, 1616, 1512, 1433, 1392, 1258. ¹H NMR (400 MHz, Chloroform-*d*) δ 8.24 (dd, *J* = 8.0, 2.0 Hz, 1H), 8.21 (s, 1H), 7.91 (s, 1H), 7.88 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.81 (s, 1H), 7.78 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.51–7.41 (m, 2 H), 4.34–4.17 (m, 10 H), 2.02–1.88 (m, 8 H), 1.88–1.79 (m, 2 H), 1.66–1.52 (m, 10 H), 1.50–1.33 (m, 16 H), 1.28 (qt, *J* = 6.5, 3.4 Hz, 4 H), 1.00–0.89 (m, 12 H), 0.88–0.81 (m, 3 H). ¹³C NMR (101 MHz, CDCl₃) δ 164.09, 149.82, 149.42, 149.28, 148.99, 148.84, 139.71, 134.73, 133.20, 132.35, 131.11, 128.18, 127.23, 124.74, 123.52, 123.20, 123.02, 122.68, 116.82, 108.09, 107.34, 106.98, 106.64, 106.08, 77.34, 77.02, 76.70, 69.95, 69.83, 69.53, 69.28, 68.94, 31.70, 31.65, 31.60, 30.93, 29.45, 29.40, 29.33, 25.87, 25.82, 25.78, 22.67, 22.56, 14.06, 13.98. MS (MALDI): *m/z* calculated for C₅₅H₇₅BrO₇ (M+, 100%): 928.10 found 928.00.

(3-Bromobenzoate) ester **8b**

Prepared from MHT and 3-bromobenzoyl chloride following the procedure described for **8a**, giving dyad **8b** as an off-white solid (0.07 g, 39%). IR (thin film, cm⁻¹) 2956, 2920, 2855, 2364, 1736, 1620, 1517, 1434, 1393, 1281, 1245. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.45 (t, *J* = 2.0 Hz, 1H), 8.22 (dt, *J* = 8.0, 2.0 Hz, 2 H), 8.19 (s, 1H), 7.91 (s, 1H), 7.88 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.81–7.78 (m, 2 H), 7.43 (t, *J* = 8.0 Hz, 1H), 4.32–4.16 (m, 10 H), 2.06–1.90 (m, 8 H), 1.86–1.72 (m, 2 H), 1.71–1.50 (m, 10 H), 1.48–1.36 (m, 16 H), 1.28–1.18 (m, 4 H), 1.02–0.88 (m, 12 H), 0.82 (t, *J* = 7.0 Hz, 3 H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 163.82, 149.81, 149.37, 148.97, 148.83, 139.86, 136.45, 133.25, 131.58, 130.16, 128.87, 128.18, 124.71, 123.46, 123.25, 123.20, 122.98, 122.68, 116.70, 107.99, 107.31, 106.93, 106.37, 69.90, 69.83, 69.52, 69.18, 69.03, 31.72, 31.66, 31.51, 29.46, 29.42, 29.34, 29.24, 25.89, 25.87, 25.83, 25.72, 22.69, 22.66, 22.56, 14.08, 14.06, 13.95. MS (MALDI): *m/z* calculated for C₅₅H₇₅BrO₇ (M+, 100%): 928.10 found 928.00.

(4-Nitrobenzoate) ester **8c**

Prepared from MHT and 4-nitrobenzoyl chloride following the procedure described for **8a**, giving dyad **8c** as an off-white solid (0.058 g, 32%). IR (thin film, cm⁻¹) 2924, 2856, 1740, 1614, 1514, 1435, 1387, 1345, 1258. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.48 (d, *J* = 8.8 Hz, 2 H), 8.40 (d, *J* = 8.8 Hz, 2 H), 8.22 (s, 1H), 7.93 (s, 1H), 7.88 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.79 (s, 1H), 4.29–4.15 (m, 10 H), 2.00–1.88 (m, 8 H), 1.79–1.72 (m, 2 H), 1.63–1.52 (m, 10 H), 1.47–1.34 (m, 16 H), 1.26–1.19 (m, 4 H), 1.08–0.88 (m, 12 H), 0.80 (t, *J* = 7.0 Hz, 3 H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 163.30, 150.88, 149.91, 149.30, 149.09, 148.87, 139.57, 135.05, 131.39, 128.34, 124.77, 123.73, 123.34, 123.28, 123.22, 122.87, 116.56, 107.99, 107.24, 106.86, 106.45, 106.25, 69.92, 69.79, 69.50, 69.24, 68.91, 31.72, 31.66, 31.45, 29.47, 29.45, 29.42, 29.35, 29.18, 25.90, 25.87, 25.84, 25.66, 22.69, 22.66, 22.55, 14.08, 14.06, 13.92. MS (MALDI): *m/z* calculated for C₅₅H₇₅NO₉ (M+, 100%): 894.20 found 893.6.

(4-Methoxybenzoate) ester **8d**

Prepared from MHT and 4-methoxybenzoyl chloride following the procedure described for **8a**, giving dyad **8d** as an off-white solid (0.03 g, 17%). IR (thin film, cm⁻¹) 2928, 2854, 1721, 1605, 1511, 1468, 1434, 1392, 1316, 1253. ¹H NMR (500 MHz, Chloroform-*d*) δ 8.25 (d, *J* = 8.9 Hz, 2 H), 8.20 (s, 1H), 7.91 (s, 1H), 7.88 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.80 (s, 1H), 7.02 (d, *J* = 8.9 Hz, 2 H), 4.33–4.15 (m, 10 H), 3.93 (s, 3 H), 2.04–1.88 (m, 8 H), 1.86–1.69 (m, 2 H), 1.62–1.50 (m, 10 H), 1.47–1.32 (m, 16 H), 1.25–1.18 (m, 4 H), 0.95–0.88 (m, 12 H), 0.82 (t, *J* = 6.5 Hz, 3 H). ¹³C NMR (126 MHz, Chloroform-*d*) δ 164.89, 163.85, 149.68, 149.23, 148.86, 148.79, 140.29, 132.43, 127.92, 124.61, 123.56, 123.28, 123.14, 123.08, 121.97, 116.95, 113.82, 107.96, 107.30, 106.94, 106.41, 77.31, 77.05, 76.80, 69.86, 69.82, 69.52, 69.15, 69.06, 55.52, 31.73, 31.67, 31.53, 29.47, 29.43, 29.35, 29.27, 25.89, 25.83, 25.66, 22.69, 22.66, 22.55, 14.08, 14.05, 13.96. MS (MALDI): *m/z* calculated for C₅₆H₇₈O₈ (M+, 100%): 878.56 found 878.06.

(1-Naphthoate) ester **8e**

Prepared from MHT and 1-naphthoyl chloride following the procedure described for **8a**, giving dyad **8e** as an off-white solid (0.116 g, 64%). IR (thin film, cm⁻¹) 2926, 2855, 1727, 1616, 1511, 1467, 1433, 1391, 1285. ¹H NMR (500 MHz, Chloroform-*d*) δ 9.11 (d, *J* = 8.7 Hz, 1H),

8.59 (dd, $J = 8.0, 1.3$ Hz, 1H), 8.26 (s, 1H), 8.14 (d, $J = 8.0$ Hz, 1H), 7.96 (d, $J = 8.0$ Hz, 1H), 7.94 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.69–7.57 (m, 3 H), 4.32–4.16 (m, 10 H), 2.04–1.88 (m, 8 H), 1.84–1.74 (m, 2 H), 1.66–1.50 (m, 10 H), 1.47–1.33 (m, 16 H), 1.25–1.11 (m, 4 H), 1.01–0.83 (m, 12 H), 0.73 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.92, 149.78, 149.67, 149.29, 148.93, 148.83, 140.12, 134.04, 133.95, 131.72, 131.23, 128.60, 128.09, 128.00, 126.39, 126.35, 126.05, 124.71, 124.59, 123.58, 123.29, 123.19, 123.09, 117.00, 108.08, 107.36, 106.97, 106.51, 106.13, 77.29, 77.03, 76.78, 69.94, 69.84, 69.53, 69.20, 68.95, 31.71, 31.65, 31.50, 29.47, 29.45, 29.42, 29.33, 25.89, 25.86, 25.81, 25.73, 22.69, 22.64, 22.45, 14.08, 14.04, 13.86. MS (MALDI): m/z calculated for $\text{C}_{59}\text{H}_{78}\text{O}_7$ (M^+ , 100%): 898 found 898.

(2-Naphthoate) ester 8 f

Prepared from MHT and 2-naphthoyl chloride following the procedure described for **8a**, giving dyad **8 f** as an off-white solid (0.05 g, 28%). IR (thin film, cm^{-1}) 2930, 2853, 1731, 1614, 1515, 1434, 1391, 1285. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.29 (dd, $J = 8.5, 1.7$ Hz, 2 H), 8.26 (s, 1H), 8.04 (d, $J = 8.5$ Hz, 1H), 7.99 (d, $J = 8.5$ Hz, 1H), 7.95 (d, $J = 8.5, 1\text{H}$), 7.93 (s, 1H), 7.90 (s, 1H), 7.84 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.66 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 7.60 (ddd, $J = 8.2, 6.9, 1.3$ Hz, 1H), 4.29–4.16 (m, 10 H), 2.00–1.86 (m, 8 H), 1.81–1.72 (m, 2 H), 1.64–1.48 (m, 10 H), 1.45–1.30 (m, 16 H), 1.26–1.09 (m, 4 H), 1.01–0.85 (m, 12 H), 0.72 (t, $J = 7.1$ Hz, 3 H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.32, 149.76, 149.64, 149.29, 148.93, 148.84, 140.27, 135.87, 132.62, 132.02, 129.52, 128.55, 128.38, 128.07, 127.87, 126.82, 126.80, 125.71, 124.69, 123.57, 123.33, 123.19, 123.08, 116.91, 108.02, 107.36, 106.99, 106.47, 106.43, 77.28, 77.23, 77.03, 76.77, 69.91, 69.84, 69.54, 69.18, 69.08, 31.71, 31.63, 31.45, 29.46, 29.45, 29.42, 29.32, 29.24, 25.88, 25.86, 25.80, 25.66, 22.68, 22.63, 22.48, 14.07, 14.03, 13.84. MS (MALDI): m/z calculated for $\text{C}_{59}\text{H}_{78}\text{O}_7$ (M^+ , 100%): 898 found 898.

(2-Anthracenoate) ester 8 g

Prepared from MHT and 2-anthracenoyl chloride following the procedure described for **8a**, giving dyad **8 g** as a green solid (0.03 g, 16%). IR (thin film, cm^{-1}) 2923, 2851, 1728, 1616, 1511, 1433, 1384, 1311, 1258. ^1H NMR (500 MHz, Chloroform-*d*) δ 9.11 (s, 1H), 8.65 (s, 1H), 8.52 (s, 1H), 8.29 (s, 1H), 8.22 (dd, $J = 8.5, 1.7$ Hz, 1H), 8.13 (d, $J = 8.0$ Hz, 1H), 8.07 (t, $J = 7.7$ Hz, 2 H), 7.95 (s, 1H), 7.91 (s, 1H), 7.85 (s, 1H), 7.86 (2 x s, 2 H), 7.60–7.51 (m, 2 H), 4.34–4.17 (m, 10 H), 2.06–1.91 (m, 8 H),

1.87–1.73 (m, 2 H), 1.71–1.55 (m, 10 H), 1.50–1.31 (m, 16 H), 1.25–1.12 (m, 4 H), 1.02–0.85 (m, 12 H), 0.72 (t, $J = 7.1$ Hz, 3 H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 165.34, 149.30, 133.38, 133.31, 132.89, 132.10, 130.46, 128.96, 128.69, 128.55, 128.24, 126.75, 126.34, 125.99, 124.70, 124.39, 116.95, 106.48, 77.27, 77.02, 76.77, 69.91, 69.85, 69.55, 69.18, 69.12, 31.71, 31.63, 31.44, 29.45, 29.42, 29.31, 29.25, 25.88, 25.85, 25.80, 25.67, 22.68, 22.62, 22.48, 14.07, 14.02, 13.83. MS (MALDI): m/z calculated for $\text{C}_{63}\text{H}_{80}\text{O}_7$ (M^+ , 100%): 948 found 948 (cluster).

(9-Anthracenoate) ester 8 h

MHT (150 mg, 0.0002 mol), anthracene-9-carboxylic acid (0.07 g, 0.0003 mol, 2.4 eq), DMAP (0.004 g, 0.000038 mol, 0.19 eq) and DCC (0.082 g, 0.049 mol, 2.4 eq) were stirred in dry CH_2Cl_2 (20 ml) under N_2 at 0 °C. After 2 days the reaction was stopped and the solvent evaporated. The residue was purified by column chromatography (silica gel, DCM/ pet. ether 2:1) and recrystallised from 2-propanol to give the **8 h** as an off-white solid (0.044 g, 23%). IR (thin film, cm^{-1}) 2922, 2855, 1739, 1615, 1513, 1467, 1432, 1389, 1353, 1257. ^1H NMR (500 MHz, Chloroform-*d*) δ 8.70 (d, $J = 8.7$ Hz, 2 H), 8.64 (s, 1H), 8.28 (s, 1H), 8.10 (d, $J = 8.7$ Hz, 2 H), 8.04 (s, 1H), 7.95 (s, 1H), 7.86 (s, 1H), 7.85 (s, 1H), 7.85 (s, 1H), 7.68–7.53 (m, 4 H), 4.43 (t, $J = 6.6$ Hz, 2 H), 4.31 – 4.17 (m, 8 H), 2.09–2.04 (m, 2 H), 2.01–1.86 (m, 8 H), 1.67–1.52 (m, 10 H), 1.49–1.35 (m, 16 H), 1.33–1.18 (m, 4 H), 1.02–0.76 (m, 15 H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.29, 149.94, 149.78, 149.30, 149.15, 148.89, 139.71, 131.08, 130.31, 129.28, 128.67, 128.39, 127.11, 126.71, 125.80, 125.58, 124.84, 123.49, 123.39, 123.32, 123.06, 116.90, 108.28, 107.42, 106.99, 106.04, 77.28, 77.02, 76.77, 70.06, 69.84, 69.52, 69.49, 69.21, 31.74, 31.71, 31.67, 31.65, 29.56, 29.49, 29.44, 29.42, 29.35, 25.90, 25.87, 25.84, 25.82, 22.70, 22.69, 22.65, 22.55, 14.08, 14.04, 13.97. (MALDI): m/z calculated for $\text{C}_{63}\text{H}_{80}\text{O}_7$ (M^+ , 100%): 948 found 950 (cluster).

Phthalate dyad 12

3,6,7,10,11-Pentakis(hexyloxy)triphenylen-2-ol MHT (0.530 g, 7.11×10^{-4} mol), benzene-1,2-dicarboxylic acid (0.046 g, 2.74×10^{-4} mol), *N,N'*-dicyclohexylcarbodiimide (DCC) (0.280 g, 1.36×10^{-3} mol) and 4-(dimethylamino)pyridine (DMAP) (0.004 g, 3.36×10^{-5} mol) were stirred in dry DCM (50 ml) at 30 °C for 72 h. The mixture was filtered, washed with dilute 2 M HCl (20 ml x 2), washed with dilute sodium hydroxide and finally

washed with distilled water and extracted with DCM (3x50 ml), dried with MgSO_4 and evaporated to dryness in vacuo. The crude product was loaded onto a silica column and eluted with a 1:20 mixture of ethylacetate/hexane. The solid obtained was recrystallised from DCM/ethanol giving the dyad **12** (0.18 g, 41%). Mp 82°C; IR (thin film, cm^{-1}) 2929, 2858, 1738, 1616, 1509, 1432, 1259; ^1H -NMR (500 MHz, Chloroform-*d*) δ 8.31 (s, 2 H), 8.17–8.15 (m, 2 H), 7.92 (s, 2 H), 7.87 (s, 2 H), 7.80 (s, 2 H), 7.76–7.74 (m, 2 H), 7.72 (s, 2 H), 7.50 (s, 2 H), 4.26–4.18 (m, 16 H), 4.09 (t, $J = 6.5$, 4 H) 2.00–1.77 (m, 20 H), 1.60–0.89 (m, 90 H) ppm. ^{13}C -NMR (126 MHz, Chloroform-*d*); δ 166.0, 150.0, 149.8, 139.9, 132.2, 131.7, 129.9, 128.4, 125.0, 123.7, 123.5, 123.0, 117.2, 108.1, 107.8, 69.6, 68.5, 31.9, 29.6, 25.8, 22.7, 14.2 ppm. MS (MALDI): m/z Calculated for $\text{C}_{104}\text{H}_{146}\text{O}_{14}$ (M^+ , 100%): 1620.07 found 1619.45.

Isophthalate twin 9

Prepared following an identical procedure to dyad **12**, giving dyad **9** (0.13 g, 29%). IR (thin film, cm^{-1}) 2954, 2858, 2928, 1741, 1616, 1511, 1432, 1260, 1225; ^1H -NMR (500 MHz, Chloroform-*d*) δ 9.16(s, 1H), 8.51 (dd, $J = 7.7$, 1.5 Hz, 2 H), 8.18 (s, 2 H), 7.87 (s, 2 H), 7.82 (s, 2 H), 7.77 (s, 2 H), 7.76 (s, 2 H), 7.74 (s, 2 H), 7.69 (t, $J = 7.7$, 1H), 4.10–4.20 (m, 20 H), 1.80–1.92 (m, 16 H), 1.69–1.76 (m, 4H), 1.25–1.41 (m, 20 H), 1.12–1.24 (m, 10 H) 0.70–0.92 (M, 30 H) ppm. ^{13}C -NMR (126 MHz, Chloroform-*d*); δ 164.2, 149.8, 148.9, 139.9, 128.2, 124.7, 123.5, 123.3, 123.2, 116.8, 108.0, 107.0, 106.4, 69.9, 69.8, 69.2, 69.0, 31.7, 31.5, 29.6, 29.0, 25.8, 22.7, 22.6, 22.3, 14.1 ppm. MS (MALDI): m/z calculated for $\text{C}_{104}\text{H}_{146}\text{O}_{14}$ (M^+ , 100%): 1620.07 found 1620.38

The urea adduct **10** was also isolated from this reaction (0.22 g, 51%). Mp 95°C; IR (thin film, cm^{-1}) 2930, 2857, 1738, 1651, 1514, 1437, 1258. ^1H -NMR (500 MHz, Chloroform-*d*) δ 8.48 (t, $J = 1.0$, 1H), 8.40–8.35(m, 1H), 8.20 (s, 1H), 7.92 (s, 1H), 7.88 (s, 1H), 7.86–7.82 (m, 3H), 7.79 (s, 1H), 7.60 (t, $J = 8.0$ Hz, 1H), 4.27–4.05 (m, 11 H), 3.61–3.53 (m, 1H) 2.12–1.19 (m, 60 H), 0.96–0.81 (m, 15 H) ppm. ^{13}C -NMR (126 MHz, Chloroform-*d*) δ 174.5, 164.3, 154.1, 149.5, 149.1, 149.0, 140.0, 137.7, 132.4, 132.0, 130.2, 129.0, 128.8, 128.3, 123.6, 123.1, 116.9, 108.2, 107.5, 107.1, 106.6, 106.5, 70.1, 69.9, 69.7, 69.7, 58.0, 49.9, 31.8, 29.6, 26.4, 26.0, 22.8, 22.7, 14.2, 14.1 ppm. MS (MALDI): m/z $\text{C}_{69}\text{H}_{99}\text{N}_2\text{O}_9$ ($\text{M} + \text{H}^+$): 1099.74 found 1099.55

Terephthalate twin 13

Prepared following an identical procedure to dyad **12**, giving dyad **13** (0.15 g, 35%). IR (thin film, cm^{-1}) 2918, 2850, 1731, 1515, 1435, 1261; ^1H -NMR (500 MHz, Chloroform-*d*) δ 8.46 (s, 4H), 8.24 (s, 2 H), 7.92 (s, 2 H), 7.88 (s, 2 H), 7.82 (s, 2 H), 7.79 (s, 4H), 4.19–4.28 (m, 20 H), 1.99–1.89 (m, 16 H), 1.76–1.84 (m, 4H), 1.52–1.65 (m, 20 H), 1.35–1.48 (m, 40 H), 0.87–0.98 (m, 30 H) ppm. ^{13}C -NMR (126 MHz, Chloroform-*d*); δ 164.5, 149.8, 149.5, 148.9, 140.0, 133.8, 130.3, 128.4, 124.9, 123.4, 123.1, 116.9, 108.2, 106.5, 69.4, 69.2, 31.9, 29.6, 25.8, 22.8, 14.1 ppm. MS (MALDI): m/z calculated for $\text{C}_{104}\text{H}_{146}\text{O}_{14}$ (M^+ , 100%): 1620.07 found 1619.68.

Thiophene Dyad 14

2,5-Thiophenedicarboxylic acid (19.2 mg, 0.001 mmol, 1eq) was dissolved in 10 ml dry DCM. Then 2 drops of dry DMF and oxalyl chloride (0.3 ml) were added to the solution. The mixture was stirred under nitrogen overnight. After that the solvents were evaporated under reduced pressure the resulting product was used straight away without further analysis.

MHT (0.25 g, 0.33 mmol, 3eq) was dissolved in dry DCM (10 ml). Then 2,5thiophenedicarbonyl dichloride (0.02 g, 0.0009 mmol, 1eq) was added to the MHT solution after dissolving it in dry DCM (10 ml). Then dry TEA (0.1 ml) was added. The reaction was kept stirring under nitrogen overnight then quenched by adding more DCM and water. The mixture was separated and washed with dilute HCl. The solvent was evaporated, and the product recrystallised from ethanol to yield dyad 14 as a pale yellow solid (0.13 g, 30%). IR (thin film, cm^{-1}) 2981, 1725, 1514, 1262. ^1H -NMR (500 MHz, Chloroform-*d*) δ 8.24 (s, 2 H), 8.09 (s, 2 H), 7.93 (s, 2 H), 7.89 (s, 2 H), 7.84–7.81 (m, 6H), 4.27–4.21 (m, 20 H), 1.97–1.82 (m, 20 H), 1.58–1.52 (m, 20), 1.30–1.41 (m, 40), 0.96–0.87 (m, 30 H) ppm. ^{13}C -NMR (126 MHz; Chloroform-*d*) 158.84, 148.8, 148.29, 148.00, 147.38, 138.44, 137.86, 133.23, 127.32, 123.76, 122.20, 115.75, 107.02, 105.94, 105.40, 68.91, 68.80, 68.51, 68.09, 30.68, 30.63, 30.50, 28.44, 28.41, 28.38, 28.31, 28.21, 24.85, 24.83, 24.80, 24.66, 21.65, 21.63, 21.57, 13.04, 13.02 ppm. MS (MALDI): m/z calculated for $\text{C}_{102}\text{H}_{144}\text{O}_{14}\text{S}$ (M^+ , 100%): 1626.32 found 1626.00.

2,7-Naphthalene dyad 11

2,7 Naphthalenedicarboxylic acid (0.5 g, 4.62 mmol, 1eq) was dissolved in DCM (20 ml). Then oxalyl chloride (3.4 g, 27.7 mmol, 6eq) and DMF 2 drops were added to

the solution. The reaction was kept stirring under nitrogen overnight. The solvent was evaporated, and the crude product recrystallised from toluene to give the acid chloride as a colourless solid (0.30 g, 30%) that was used directly in the next step.

2,7-Naphthalene dicarbonyl dichloride (0.06 g, 0.268 mmol, 1eq) was dissolved in dry DCM (20 ml) then it was added to a solution of **MHT** (0.5 g, 0.670 mmol, 2.5eq) in dry DCM (20 ml) followed by dry TEA (0.1 ml). The reaction was kept stirring under nitrogen overnight then quenched by adding more DCM and water. The mixture was separated and washed with dilute HCl. The solvent was evaporated, and the product recrystallised from ethanol to yield dyad **11** as a pale yellow solid (0.2 g, 40%). IR (thin film, cm^{-1}) 2928., 1727, 1513, 1254. $^1\text{H-NMR}$ (500 MHz, Chloroform-*d*) δ 8.98 (s, 2H), 8.41 (d, $J = 8.0$ Hz, 2H), 8.28 (s, 2H), 8.18 (d, $J = 8.0$ Hz, 2H), 7.95 (s, 2H), 7.90 (s, 2H), 7.87–7.82 (m, 6H), 4.19–4.28 (m, 20 H), 1.77–1.98 (m, 20 H), 1.17–1.52 (m, 80 H), 0.73–0.98(m, 30 H). $^{13}\text{C-NMR}$ (126 MHz; Chloroform-*d*) 164.82, 149.75, 149.52, 149.17, 148.82, 148.85, 141.74, 140.14, 130.87, 130.33, 129.00, 126.83, 123.32, 117.04, 116.92, 106.87, 106.39, 69.89, 69.81, 69.56, 69.19, 69.07, 31.73, 31.67, 31.53, 29.46, 29.35, 29.27, 25.90, 25.87, 25.83, 25.69, 22.69, 22.66, 22.56, 14.08, 14.05, 13.97 ppm.

4,4'-Stilbene dyad 15

Prepared from **MHT** and stilbene-4,4'-dicarboxylic acid following the procedure described for dyad **11** to give **15** as a colourless solid (0.2 g, 50%). IR (thin film, cm^{-1}) 2915, 2850, 1729, 1509, 1432, 1256. $^1\text{H-NMR}$ (500 MHz, Chloroform-*d*) δ 8.33 (d, $J = 8.4$ Hz, 4H), 8.23 (s, 2H), 7.94 (d, $J = 8.4$ Hz, 4H), 7.89–7.71 (m, 10 H), 7.38 (s, 2H), 4.33–4.15 (m, 20 H), 2.02–1.74 (m, 20 H), 1.65–1.15 (m, 65 H), 1.00–0.77 (m, 30 H). $^{13}\text{C-NMR}$ (126 MHz; Chloroform-*d*) 165.79, 161.50, 149.86, 149.41, 149.05, 148.96, 146.52, 140.24, 130.18, 128.08, 127.73, 126.99, 125.98, 124.79, 123.73, 123.31, 123.24, 115.09, 108.17, 107.15, 103.66, 77.41, 77.16, 76.91, 70.05, 69.99, 69.68, 69.34, 69.27, 68.38, 31.84, 31.79, 31.70, 29.58, 29.55, 29.46, 29.42, 29.28, 26.01, 25.99, 25.96, 25.84, 22.81, 22.79, 22.75, 14.20, 14.13 ppm.

Triad 16

1, 3, 5-Benzene tricarbonyl chloride (0.03 g, 0.0001 mmol, 1eq) was dissolved in dry DCM (10 ml) and added to a solution of **MHT** (0.4 g, 0.536 mmol, 4.5 eq) in dry DCM (10 ml) and TEA (1 ml). The mixture

was stirred under nitrogen overnight at room temperature then quenched by adding more DCM and water. The mixture was separated and washed with dilute HCl. The solvent was evaporated then the crude was purified by column chromatography on silica gel eluting with ethyl acetate and petroleum ether (1:15) to give triad **16** as a pale yellow solid (0.09 g, 32%). IR (thin film, cm^{-1}) 2919.83, 1742.70, 1263.73 $^1\text{H-NMR}$ (500 MHz, CD_3COCD_3) δ 9.42(s,3H), 8.21(s,3H), 7.69 (s,3H), 7.78 (s,3H), 7.51(s,3H), 7.20(s,3H), 6.97(s,3H), 3.77–4.36 (m,30 H), 1.41–2.09(m,120 H), 0.88–1.04(m, 45 H). $^{13}\text{C-NMR}$ (126 MHz; CD_3COCD_3) δ = 163.36, 148.33, 139.39, 139.23, 131.21, 123.20, 122.81, 107.15, 106.33, 69.80, 68.84, 31.81, 31.72, 31.54, 30.93, 29.63, 29.45, 29.33, 29.25, 26.00, 25.88, 25.81, 25.63, 22.73, 22.63, 22.50, 14.11, 14.08, 14.01, 13.91 ppm. MS (MALDI): m/z calculated for $\text{C}_{153}\text{H}_{216}\text{O}_{21}$ (M^+ , 100%): 2391 found 2392 (cluster).

Conclusions

A short series of monomeric triphenylenes bearing a single aryl ester plus five hexyloxy substituents has been synthesised and investigated. All examples form columnar hexagonal mesophases and the stability of the mesophases is relatively insensitive to the ester employed. Ester linked dyad systems have been prepared from diacids and several examples, which can be considered to have intermediate rigidity between columnar alkoxy-bridged systems and nematic dialkynes, show narrow-range nematic phases which further implies that a combination of shape and rigidity are necessary to promote nematic behaviour over columnar organisation. The corresponding triad based on benzene-1,3,5-triester linkage is non-mesogenic.

Acknowledgments

We thank Princess Nourah Bint Abdul Rahman university, Taibah university, Technical and Vocational training corporation (Saudi Arabia) and TETFUND Nigeria for financial support.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by the TETFUND Nigeria; Technical and Vocational training corporation (Saudi Arabia); Princess Nourah Bint Abdul Rahman University; Taibah University.

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