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Synthesis and liquid crystal properties of mixed alkynyl-alkoxy-triphenylenes

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The synthesis and liquid crystalline properties of some new multisubstituted triphenylenes are reported. The materials bear combinations of alkyne and alkoxy substituents and were designed to probe the structural factors controlling mesophase formation, type and stability in triphenylene discotics. A combination of factors contributes to mesophase stability in these systems. Compounds bearing two alkynes can support, and indeed enhance, columnar mesophase behaviour, but mesophase behaviour is completely suppressed when four or six alkynes are present. A twinned structure linked by a diacetylene bridge shows a stable nematic phase, but conversion to a saturated bridge destroys all mesophase behaviour.

Keywords: discotics; columnar phases; triphenylenes

1. Introduction

Discotic liquid crystals based on the triphenylene core were among the first investigated and have subsequently received a great deal of interest (*1*, *2*). This arises in part because of their ability to act as one-dimensional charge transport materials, acting as photoconductors or semiconductors on doping (*3–6*) and, alongside other discotic frameworks, they lend themselves to diverse electronic and optical applications (*7–15*).

A large number of discotic materials based on triphenylene have now been reported and a particular challenge has revolved around unravelling and understanding the structural factors that control the formation of stable mesophases in these systems. Indeed the triphenylene scaffold has proved to be extremely versatile for such fundamental interrogation of structural factors controlling mesophase behaviour (stability, type, etc.). We and others have developed new and improved synthetic protocols to permit characterisation of a wide range of symmetrical (most common) and unsymmetrically substituted derivatives (*16–19*).

Through our synthesis and examination of a wide range of triphenylene derivatives we have established a set of qualitative parameters governing their mesophase formation and stability. We have concluded that the central core of such discotic molecules extends beyond the central aromatic triphenylene unit to include the attached conjugated substituents (*20*, *21*). Perturbation of this extended core has a dramatic effect on the mesophase behaviour. For example, hexaalkoxytriphenylenes (HATs), such as HAT6, are the most studied triphenylene-based discotic liquid crystals and are typically characterised as giving columnar hexagonal mesophases (Figure 1) (*22*). Replacement of one conjugating substituent with another tends to maintain the mesophase behaviour (*17*, *22–24*). However, exchange with, or addition of, a non-conjugating group tends to destroy the mesophase (*23*, *25*, *26*). We have investigated a series of triphenylenes where the alkoxy groups of parent HATs were sequentially replaced with alkyl substituents (26). The trend persists in this series and we find that all derivatives are non-mesogenic. A smaller number of alkynyl-substituted triphenylenes have been investigated. Columnar mesophase behaviour is preserved if a single alkoxy group is replaced by alkyne (*25*) whereas introduction of six alkylphenylacetylene substituents leads to formation of nematic phases (*28*).

2. Results and discussion

This paper describes the synthesis and mesophase behaviour of alkynyl-alkoxy-triphenylenes in which the number and position of substituents was sequentially varied. This series of compounds can be considered as derivatives of the parent hexahexyloxytriphenylene HAT6 where two, four or six of the hexyloxy substituents are replaced by alkyne. Two alkyne substituents were selected for investigation. Heptyne substituents were chosen so that the overall chain length remained unchanged as each hexyloxy substituent was replaced (each are seven atoms long), and hexyne chains were introduced in separate series to ensure that no significant odd-even effects were overlooked.

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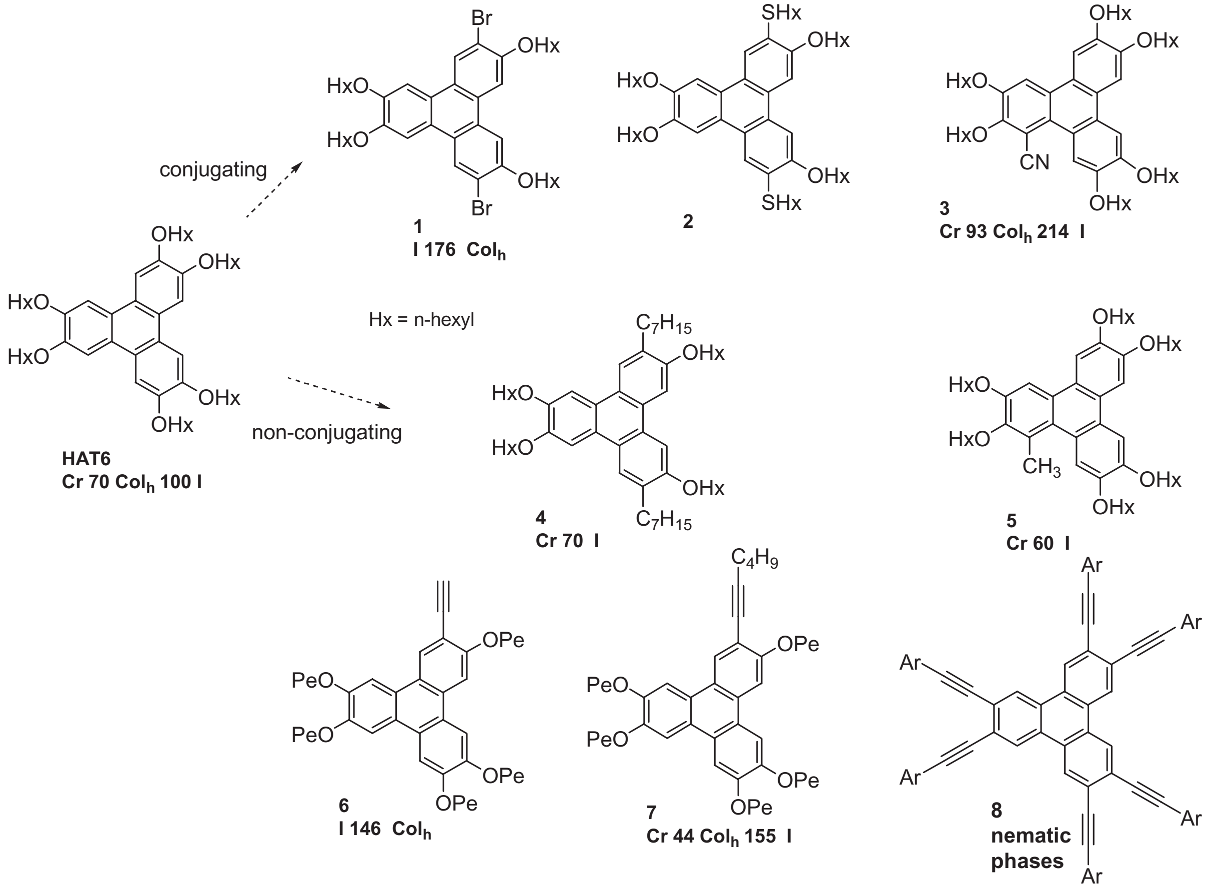


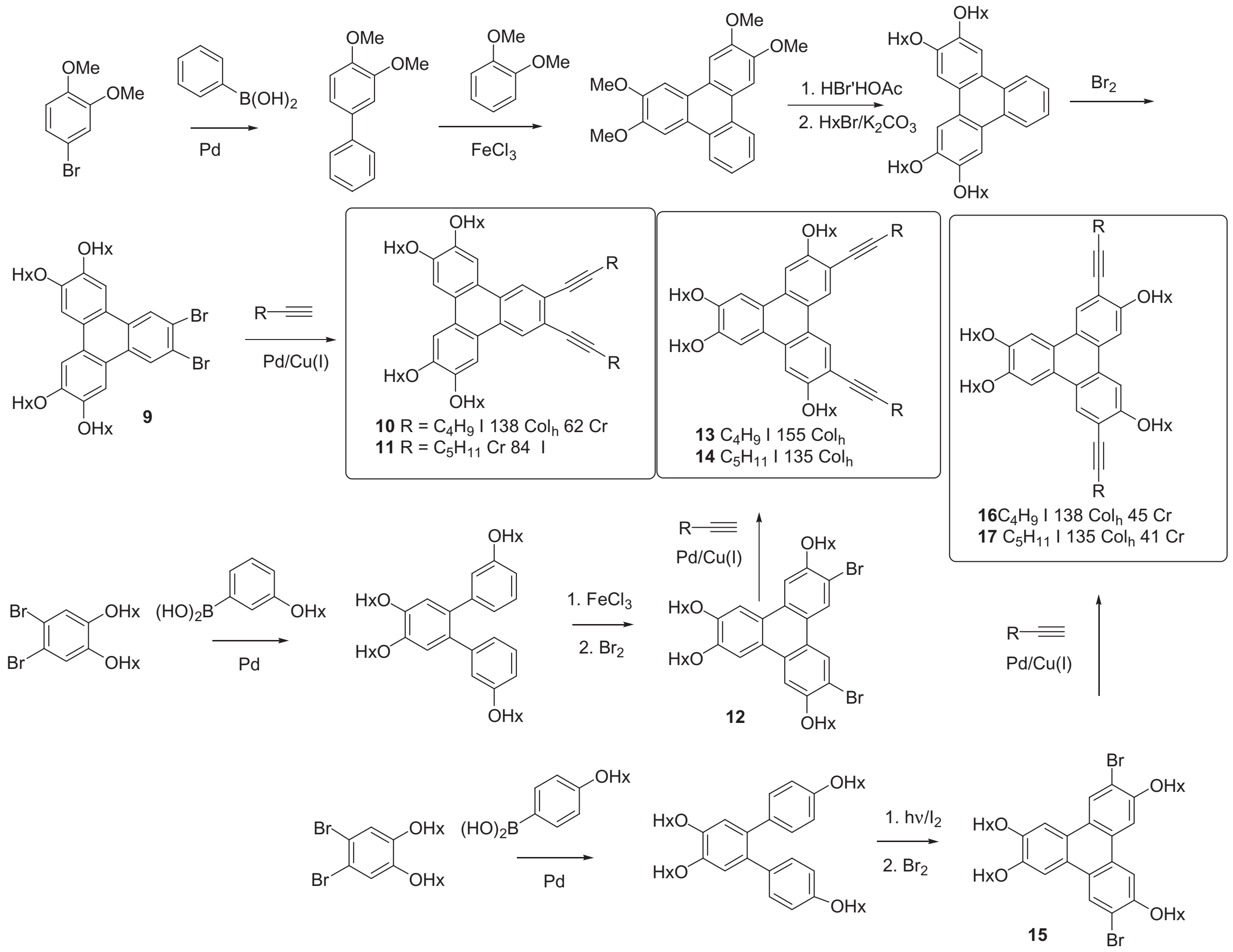
Figure 1. The effect of substituents on mesophase behaviour in triphenylene discotics.

The syntheses and mesophase behaviour of the triphenylenes bearing two alkynyl groups is shown in Scheme 1. The target dialkynes were prepared from the corresponding dibromides and 1-hexyne or 1-heptyne using palladium catalysed Sonagashira coupling conditions (*29*). Regiochemically pure dibromides were themselves prepared following our previously reported strategies (*17*).

The mesophase behaviour of the new materials was determined by polarising optical microscopy. All mesophases observed were enantiotropic and gave textures characteristic of columnar hexagonal phases. In general it can be seen that replacing two alkoxy substituents with alkynes results in overall stabilisation of the columnar mesophase by around 40–50°C. Mesophase behaviour appears relatively insensitive to the location of the alkyne substituents, although crystallisation is suppressed most in compounds **13**/**14** where the new groups are introduced into the 3,6-positions and the columnar mesophase is observed down to room temperature. Triphenylene **11** is exceptional within the series of materials investigated in that it does not form a mesophase.

The syntheses of the triphenylenes bearing four alkynyl groups are shown in Scheme 2 and followed a similar pathway via the corresponding tetrabromides (*17*). The synthesis of the symmetrical triphenylenes bearing six alkynyl groups is also shown in Scheme 2. In this case it was found most convenient to perform the final Sonagashira couplings on triphenylene hexatriflate. Derivatives bearing four alkynyl substituents do not show mesophase behaviour and melt directly into isotropic liquids. The symmetrical hexaalkynyltriphenylenes (*28*) similarly do not show formation of any mesophases and this behaviour contrasts with the known, related materials bearing alkyl-*phenyl*acetylene substituents that are known to form nematic mesophases (*28*).

It would appear therefore that the mesophase behaviour of these hybrid structures shows a rather unusual trend where the most stable mesophases are formed by compounds bearing specific combinations of the two substituents. Triphenylenes bearing five or four alkoxides with remaining positions (total of six substituents) occupied by alkynes show, in most cases, enhanced mesophase stability and range compared with the parent hexaalkoxytriphenylene. This contrasts with the



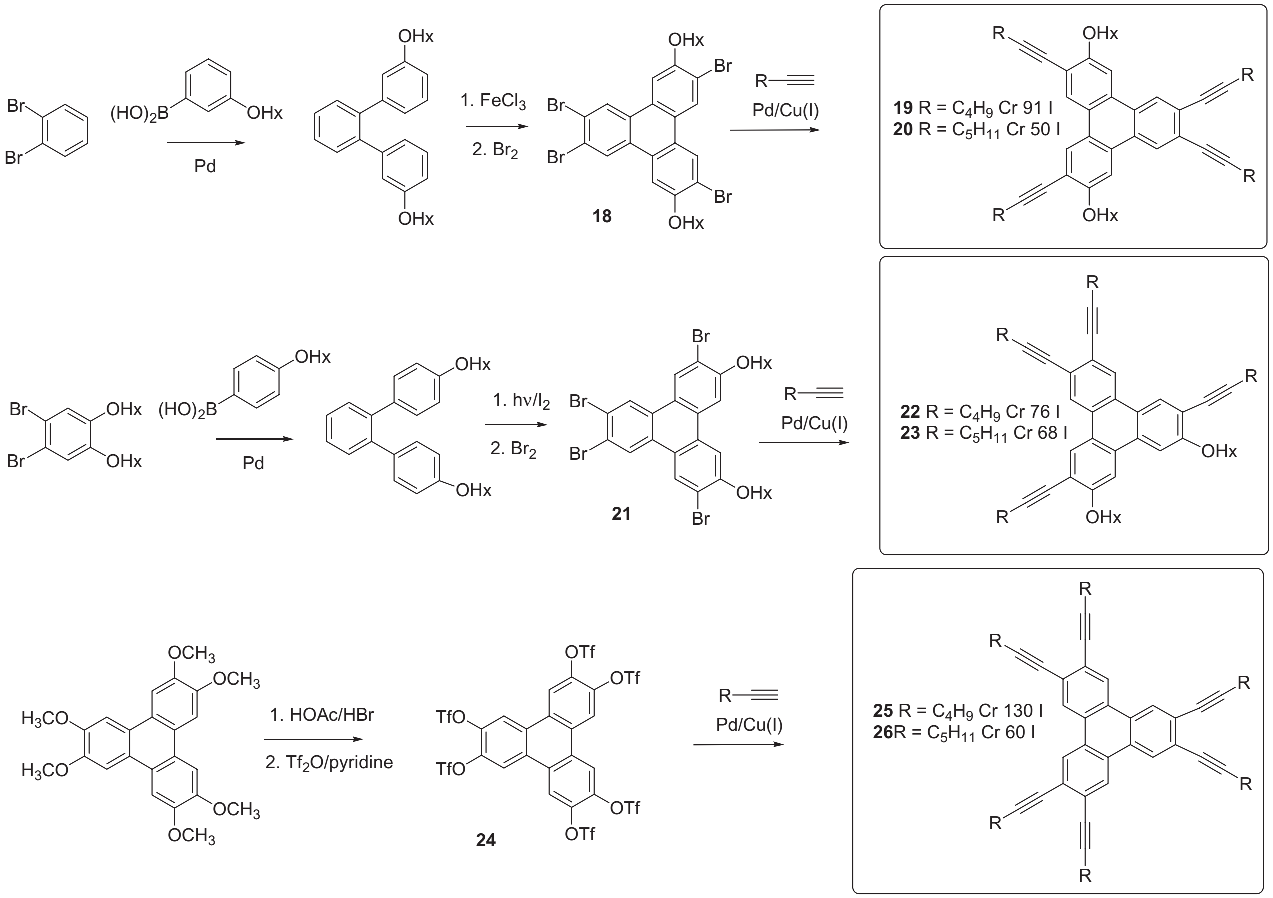
Scheme 1. Synthesis and thermal properties of dialkynyltriphenylenes.

saturated structures (bearing one or more alkyl substituents in place of one or more alkoxides) in which mesophase behaviour is destroyed. Once again these findings suggest that substituents able to conjugate with, and therefore extend, the triphenylene core are necessary for mesophase formation. However, mesophase behaviour is destroyed when four or six of the substituents are alkyne groups and this suggests that strict limitations exist to the extent to which the basic mesogenic core structure can be perturbed.

Dimeric or twinned structures have been investigated recently and an example of a diacetylene-linked triphenylene mesogen has been reported to show nematic behaviour (*30*). We were interested to probe the features of this class of material to see if the mesophase stability trends followed those found for monomeric materials. Discotic twin **27** was synthesised as previously reported (*30*). Hydrogenation using Pd/H$_2$ smoothly yielded the corresponding triphenylene twin with a saturated (butyl-) bridge **28**. Characterisation of this material revealed that this change resulted in complete destruction of mesophase behaviour, in line with our expectations for core structures bearing a non-conjugating substituent. To complete the series the corresponding alkoxide-linked twin was prepared by reaction of monohydroxypentahexyloxy triphenylene **29** with 1,2-dibromoethane. Like **27** and **28**, the resulting twin **30** has a four atom bridge (Scheme 3). The bridge is flexible and saturated (like **28**) yet links to the triphenylene cores via a conjugating substituent. This twin is also found to be non-mesogenic and we conclude that the flexible bridge suppresses nematic behaviour while it is too short to allow columnar packing.

3. Conclusions

Series of new multisubstituted triphenylenes have been synthesised and their liquid crystalline properties characterised. The materials bear combinations of alkyne- and alkoxy substituents and were designed to probe the structural factors controlling mesophase formation, type and stability in triphenylene discotics. We



Scheme 2. Synthesis and thermal properties of tetra- and hexaalkynyltriphenylenes.

concluded that a combination of factors contribute to mesophase stability in these systems. Compounds bearing two alkynes can support, and indeed enhance, columnar mesophase behaviour but mesophase behaviour is completely suppressed when four or six alkynes are present. A twinned stucture linked by a diacetylene bridge shows a stable nematic phase, but conversion to a saturated bridge destroys all mesophase behaviour.

4. Experimental

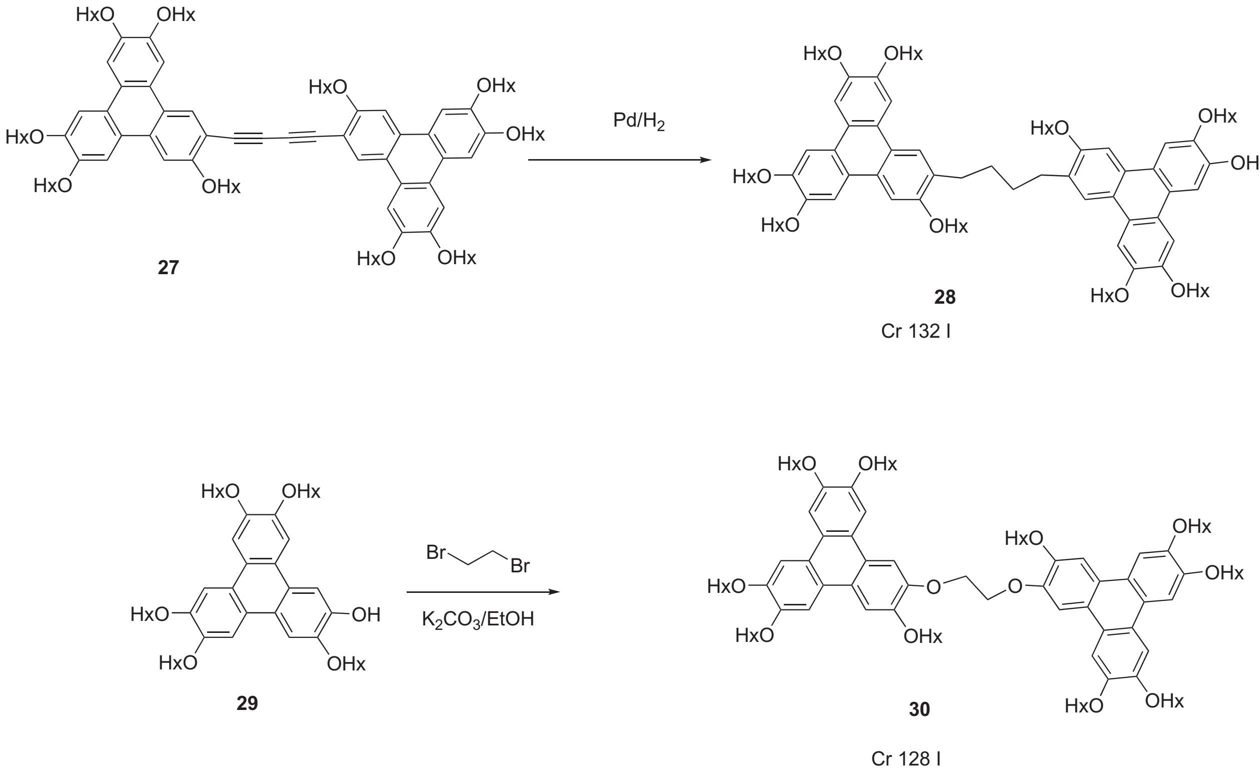
Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker EMX 400 instument. Liquid crystal properties were investigated using an Olympus BH-2 polarising microscope and Linkham TMS 92 hot stage.

4.1 General procedure for synthesis of alkynyltriphenylenes

The corresponding triphenylene bromide (or triflate), CuI, Pd(PPh$_3$)Cl$_2$ and PPh$_3$ were dissolved in triethylamine in an atmosphere of argon. The reaction mixture was heated to 100°C for 5 minutes. The corresponding aliphatic alkyne was then added and the mixture heated under reflux for a further 24 hours. The mixture was cooled down, MeOH (20 ml) added and the precipitate obtained was filtered off. The solid was dissolved in CH$_2$Cl$_2$ (50 ml), water added and the organic layer extracted with CH$_2$Cl$_2$ (3 × 20 ml). The organic extracts were dried (MgSO$_4$) and the solvent removed *in vacuo*. The crude product was purified by column chromatography (eluting with petroleum ether/CH$_2$Cl$_2$) and recrystallisation from isopropanol.

4.2 2,3,6,7-tetrakis(hexyloxy)-10,11-bis(hex-1-ynyl) triphenylene 10

The title compound was obtained using 2,3-dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene **9** (0.50 g, 0.64 mmol), CuI (0.01 g, 0.05 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.10 g, 0.14 mmol), PPh$_3$ (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-hexyne (0.52 g, 6.36 mmol). Yield: 0.18 g, 36%.



Scheme 3. Synthesis and thermal properties of saturated triphenylene twins.

Col$_h$-I 142°C; ^{1}H NMR (400 MHz, CDCl$_3$): 0.91–0.96 (m, 6H), 1.00 (t, J = 7.3, 12H), 1.38–1.62 (m, 28H), 1.67–1.72 (m, 4H), 1.90–1.97 (m, 8H), 2.58 (t, J = 6.7, 4H), 4.21–4.25 (m, 8H), 7.78 (s, 2H), 7.91 (s, 2H), 8.48 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): 13.8, 14.1, 19.6, 22.2, 22.7, 25.8, 29.4, 29.5, 31.1, 31.7, 69.5, 69.8, 80.4, 94.1, 107.3, 123.1, 123.7, 124.7, 126.7, 128.2, 149.6, 150.2; EIMS *m/z* 788.6 (M$^+$, 100%); EIHRMS *m/z* 788.5733 (expected for $C_{54}H_{76}O_4$ 788.5738).

4.3 2,3-dihept-1-ynyl-6,7,10,11-tetrakis(hexyloxy) triphenylene 11

The title compound was obtained using 2,3-dibromo-6,7,10,11-tetrakis(hexyloxy)triphenylene **9** (0.50 g, 0.64 mmol), CuI (0.01 g, 0.05 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.10 g, 0.14 mmol), PPh$_3$ (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-heptyne (0.60 g, 6.25 mmol). Yield: 0.16 g, 32%.

Mp 84°C; ^{1}H NMR (400 MHz, CDCl$_3$): 0.91–1.25 (m, 18H), 1.39–1.59 (m, 32H), 1.69–1.76 (m, 4H), 1.90–1.98 (m, 8H), 2.56 (t, J = 7.1, 4H), 4.23 (t, J = 6.6, 8H), 7.78 (s, 2H), 7.91 (s, 2H), 8.48 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): 14.0, 14.1, 19.8, 22.4, 22.7, 25.8, 28.7, 29.4, 31.3, 31.7, 69.5, 69.8, 80.3, 94.1, 107.2, 123.0, 123.6, 124.7, 126.7, 128.2, 149.5, 150.1; EIMS *m/z* 816.6 (M$^+$, 100%); EIHRMS *m/z* 816.6053 (expected for $C_{56}H_{80}O_4$ 816.6051).

4.4 2,3,6,11-tetrakis(hexyloxy)-7,10-bis(hex-1-ynyl) triphenylene 13

The title compound was obtained using 2,11-dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene **12** (1.00 g, 1.27 mmol), CuI (0.01 g, 0.05 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (0.10 g, 0.14 mmol), PPh$_3$ (0.20 g, 0.76 mmol), triethylamine (20 ml) and *n*-hexyne (1.00 g, 12 mmol). Yield: 0.33 g, 33%.

Col$_h$-I 157°C; ^{1}H NMR (400 MHz, CDCl$_3$): 0.91–0.99 (m, 18H), 1.38–1.54 (m, 32H), 1.90–1.97 (m, 8H), 2.54 (t, J = 7.3, 4H), 4.23 (t, J = 6.7, 8H), 7.70 (s, 2H), 7.83 (s, 2H), 8.52 (s, 2H); ^{13}C NMR (75 MHz, CDCl$_3$): 13.5, 13.9, 19.4, 21.9, 22.5, 22.6, 25.7, 29.3, 30.9, 31.5, 31.6, 69.1, 69.6, 94.8, 104.6, 107.6, 113.8, 122.5, 124.5, 128.4, 129.2, 149.8, 157.9; EIMS *m/z* 788.7 (M$^+$, 100%); EIHRMS *m/z* 788.5735 (expected for $C_{54}H_{76}O_4$ 788.5738).

4.5 2,11-di(hept-1-ynyl)-3,6,7,10-tetrakis(hexyloxy) triphenylene 14

The title compound was obtained using 2,11-dibromo-3,6,7,10-tetrakis(hexyloxy)triphenylene **12** (0.50 g, 0.63 mmol), CuI (0.01 g, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-heptyne (1.00 g, 12 mmol). Yield: 0.16 g, 30%.

Col_h-I 144°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.91–0.98 (m, 18H), 1.36–1.73 (m, 36H), 1.90–1.98 (m, 8H), 2.54 (t, J = 7.1, 4H), 4.23 (t, J = 6.4, 8H), 7.71 (s, 2H), 7.84 (s, 2H), 8.53 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 14.1, 19.9, 22.4, 22.7, 22.8, 25.9, 28.8, 29.5, 31.3, 31.7, 69.2, 69.7, 95.0, 104.8, 107.7, 114.0, 122.6, 124.6, 128.5, 129.4, 150.0, 158.0; EIMS *m/z* 816.7 (M^+, 100%); EIHRMS *m/z* 816.6052 (expected for $C_{56}H_{80}O_4$ 816.6051).

4.6 2,3,7,10-tetrakis(hexyloxy)-6,11-bis(hex-1-ynyl) triphenylene 16

The title compound was obtained using 2,7-dibromo-3,6,10,11-tetrakis(hexyloxy)triphenylene **15** (0.34 g, 0.43 mmol), CuI (0.01 g, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-hexyne (0.52 g, 6.36 mmol). Yield: 0.095 g, 28%.

Col_h-I 142°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.92–0.96 (m, 6H), 1.01 (t, J = 7.4, 12H), 1.25–1.73 (m, 32H), 1.90–1.98 (m, 8H), 2.57 (t, J = 6.8, 4H), 4.20–4.26 (m, 8H), 7.78 (s, 2H), 7.84 (s, 2H), 8.44 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 14.1, 19.6, 22.1, 22.7, 22.8, 25.8, 25.9, 29.4, 31.0, 31.7, 31.8, 69.3, 69.6, 95.5, 105.5, 106.7, 114.9, 123.1, 124.2, 128.4, 129.4, 149.5, 157.9; EIMS *m/z* 789.7 ($[M+H]^+$, 100%); EIHRMS *m/z* 788.5736 (expected for $C_{54}H_{76}O_4$ 788.5738).

4.7 2,7-dihept-1-ynyl-3,6,10,11-tetrakis(hexyloxy) triphenylene 17

The title compound was obtained using 2,7-dibromo-3,6,10,11-tetrakis(hexyloxy)triphenylene **15** (0.40 g, 0.5 mmol), CuI (0.01 g, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-heptyne (0.60 g, 6.25 mmol). Yield: 0.14 g, 34%.

Col_h-I 140°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.92–0.97 (m, 18H), 1.36–1.63 (m, 32H), 1.67–1.73 (m, 4H), 1.92–1.97 (m, 8H), 2.55 (t, J = 7.1, 4H), 4.20–4.26 (m, 8H), 7.77 (s, 2H), 7.83 (s, 2H), 8.48 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.9, 19.7, 22.5, 22.6, 25.7, 25.8, 28.5, 29.3, 31.5, 31.6, 69.1, 69.3, 95.3, 105.2, 106.4, 114.6, 122.8, 124.0, 128.3, 129.2, 149.3, 157.7; EIMS *m/z* 817.7 ($[M+H]^+$, 100%); EIHRMS *m/z* 816.6045 (expected for $C_{56}H_{80}O_4$ 816.6051).

4.8 2,7-bis(hexyloxy)-3,6,10,11-tetrakis(hex-1-ynyl) triphenylene 19

The title compound was obtained using 2,3,7,10-tetrabromo-6,11-bis(hexyloxy)triphenylene **18** (1.00 g, 1.34 mmol), CuI (0.02 g, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (0.20 g, 0.28 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (20 ml) and *n*-hexyne (2.00 g, 24 mmol). Yield: 0.29 g, 29%.

Mp 91°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.85–1.02 (m, 18H), 1.25–1.44 (m, 28H), 1.91–1.97 (m, 4H), 2.52–2.59 (m, 8H), 4.24 (t, J = 6.4, 4H), 7.08 (s, 2H), 8.48 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.7, 13.8, 14.1, 19.6, 22.1, 22.2, 22.7, 25.8, 29.4, 31.0, 31.1, 31.8, 69.2, 80.1, 94.8, 95.7, 104.9, 115.3, 123.4, 124.9, 127.2, 128.4, 128.7, 128.9, 158.3; EIMS *m/z* 748.7 (M^+, 100%); EIHRMS *m/z* 748.5218 (expected for $C_{54}H_{68}O_2$ 748.5214).

4.9 2,3,7,10-tetrakis(hept-1-ynyl)-6,11-bis(hexyloxy) triphenylene 20

The title compound was obtained using 2,3,7,10-tetrabromo-6,11-bis(hexyloxy)triphenylene **18** (1.00 g, 1.34 mmol), CuI (0.02 g, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (0.20 g, 0.28 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (20 ml) and *n*-heptyne (3.00 g, 32 mmol). Yield: 0.29 g, 27%.

Mp 50°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.93–0.98 (m, 18H), 1.37–1.63 (m, 28H), 1.67–1.75 (m, 8H), 1.93–1.97 (m, 4H), 2.52–2.58 (m, 8H), 4.23 (t, J = 6.6, 4H), 7.80 (s, 2H), 8.49 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 19.9, 22.4, 22.7, 25.8, 28.6, 29.4, 29.8, 31.2, 31.3, 31.8, 69.1, 80.1, 94.9, 95.8, 104.8, 115.3, 123.4, 124.9, 127.1, 128.3, 128.6, 128.9, 158.3; EIMS *m/z* 804.7 (M^+, 100%); EIHRMS *m/z* 804.5855 (expected for $C_{58}H_{76}O_2$ 804.5840).

4.10 2,11-bis(hexyloxy)-3,6,7,10-tetrakis(hex-1-ynyl)-triphenylene 22

The title compound was obtained using 2,3,6,11-tetrabromo-7,10-bis(hexyloxy)triphenylene **21** (0.40 g, 0.54 mmol), CuI (0.01 g, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-hexyne (1.50 g, 17 mmol). Yield: 0.092 g, 23%.

Mp 76°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.93–1.26 (m, 18H), 1.37–1.71 (m, 28H), 1.93–1.97

(m, 4H), 2.55 (t, *J* = 7.1, 8H), 4.23 (t, *J* = 6.6, 4H), 7.69 (s, 2H), 8.48 (s, 2H), 8.52 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 12.7, 13.0, 18.5, 18.6, 21.0, 21.1, 21.7, 24.9, 28.4, 28.7, 29.9, 30.0, 30.1, 68.1, 79.1, 93.1, 94.8, 103.9, 114.1, 122.1, 123.2, 125.5, 126.5, 128.1, 129.3, 157.8; EIMS *m/z* 748.7 (M^+, 100%); EIHRMS *m/z* 748.5217 (expected for $C_{54}H_{68}O_2$ 748.5214).

4.11 2,3,6,11-tetrakis(hept-1-ynyl)-7,10-bis(hexyloxy) triphenylene 23

The title compound was obtained using 2,3,6,11-tetrabromo-7,10-bis(hexyloxy)triphenylene **21** (0.40 g, 0.54 mmol), CuI (0.01 g, 0.05 mmol), $Pd(PPh_3)_2Cl_2$ (0.10 g, 0.14 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-heptyne (1.00 g, 12 mmol). Yield: 0.11 g, 26%.

Mp 68°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.93–1.26 (m, 18H), 1.37–1.75 (m, 36H), 1.94–1.97 (m, 4H), 2.54 (t, *J* = 7.1, 8H), 4.24 (t, *J* = 6.6, 4H), 7.72 (s, 2H), 8.50 (s, 2H), 8.55 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.0, 18.8, 18.9, 21.3, 21.4, 21.6, 24.8, 27.6, 27.7, 28.3, 30.2, 30.3, 30.7, 68.2, 79.0, 93.3, 94.9, 104.1, 114.3, 122.2, 123.3, 125.6, 128.2, 129.3, 157.8; EIMS *m/z* 804.7 (M^+, 100%); EIHRMS *m/z* 804.5848 (expected for $C_{58}H_{76}O_2$ 804.5840).

4.12 2,3,6,7,10,11-hexa(hex-1-ynyl)triphenylene 25

The title compound was obtained using triphenylene-2,3,6,7,10,11-hexatriflate **24** (1.00 g, 0.98 mmol), CuI (0.02 g, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (0.20 g, 0.28 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-hexyne (0.78 g, 9.8 mmol). Yield: 0.17 g, 25%.

Mp 130°C; ^{1}H NMR (400 MHz, $CDCl_3$): 1.00 (t, *J* = 7.3, 18H), 1.55–1.65 (m, 12H), 1.67–1.70 (m, 12H), 2.58 (t, *J* = 7.1, 12H), 8.52 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.5, 19.3, 21.9, 30.8, 79.5, 95.0, 125.4, 126.9, 127.9; EIMS *m/z* 709.6 ($[M+H]^+$, 100%); EIHRMS *m/z* 708.4688 (expected for $C_{54}H_{60}$ 708.4690).

4.13 2,3,6,7,10,11-hexa(hept-1-ynyl)triphenylene 26

The title compound was obtained using triphenylene-2,3,6,7,10,11-hexatriflate **24** (1.00 g, 0.98 mmol), CuI (0.02 g, 0.11 mmol), $Pd(PPh_3)_2Cl_2$ (0.20 g, 0.28 mmol), PPh_3 (0.20 g, 0.76 mmol), triethylamine (30 ml) and *n*-heptyne (0.94 g, 9.8 mmol). Yield: 0.20 g, 26%.

Mp 60°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.96 (t, *J* = 7.3, 18H), 1.38–1.56 (m, 24H), 1.67–1.72 (m, 12H), 2.54 (t, *J* = 7.1, 12H), 8.53 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): 14.0, 19.8, 22.4, 28.6, 31.3, 79.8, 95.3, 125.6, 127.2, 128.2; EIMS *m/z* 793.7 ($[M+H]^+$, 100%); EIHRMS *m/z* 792.5636 (expected for $C_{60}H_{72}$ 792.5629).

4.14 Dimer 28

Compound **27** (0.20g, 0.13 mmol) was dissolved in a mixture of tetrahydrofuran (15 ml) and ethanol (3 ml) and the solution purged with nitrogen gas. Palladium on charcoal (5 mg) was added to this solution, which was then subjected to an atmosphere of hydrogen for 24 hours at a pressure of 50 atm. The solution was then purged with nitrogen and the catalyst was filtered upon celite. The solution was concentrated *in vacuo* and the crude solid obtained purified by column chromatography (eluting with ethyl acetate/petroleum ether, 1:4) to give the pure title compound (0.16 g, 80%) as an off-white solid.

Mp 132°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.86–0.96 (m, 30H), 1.25–1.60 (m, 60H), 1.81–1.98 (m, 24H), 2.93 (t, *J* = 6.3, 4H), 4.14–4.25 (m, 20H), 7.71 (s, 2H), 7.81 (s, 2H), 7.82 (s, 2H), 7.88 (s, 2H), 7.89 (s, 2H), 8.18 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.9, 22.5, 25.7, 25.8, 29.3, 29.4, 29.6, 30.4, 31.1, 31.4, 31.5, 31.6, 67.9, 69.3, 69.5, 69.8, 103.4, 106.7, 107.1, 107.6, 107.8, 122.5, 123.0, 123.6, 124.1, 124.2, 124.5, 128.3, 131.4, 148.6, 148.8, 149.3, 149.5, 156.3; MALDI-MS *m/z* 1511 (M^+, 100%).

4.15 Dimer 30

2-Hydroxy-3,6,7,10,11-pentakis(hexyloxy)triphenylene **29** (0.50 g, 0.65 mmol), 1,2-dibromoethane (0.124 g, 0.66 mmol) and anhydrous K_2CO_3 (0.138 g, 1.0 mol) were heated in refluxing acetone (10 ml) under nitrogen for 24 hours. Dilute hydrochloric acid was added and the mixture extracted with dichloromethane (3 × 50 ml). The solvent was removed *in vacuo* and the residue purified by column chromatography (eluting with ethyl acetate/ petroleum ether, 1:4) to give the pure title compound (0.34 g, 67%).

Mp 128°C; ^{1}H NMR (400 MHz, $CDCl_3$): 0.80–0.95 (m, 30H), 1.24–1.62 (m, 60H), 1.77–1.98 (m, 20H), 4.03 (t, *J* = 6.6, 4H), 4.16–4.25 (m, 16H), 4.74 (s, 4H), 7.80–7.83 (m, 10H), 8.01 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): 13.8, 13.9, 22.4, 22.5, 25.6, 25.7, 29.2, 29.3, 31.4, 31.5, 31.6, 69.2, 69.5, 69.6, 69.7, 106.7, 107.2, 107.5, 109.8, 123.4, 123.6, 123.7, 123.9, 124.5, 148.5, 148.9, 149.0, 149.2, 149.3; MALDI-MS *m/z* 1516 (M^+, 100%).

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