Stabilised columnar mesophases formed by 1:1 mixtures of hexaalkoxytriphenylenes with a hexaphenyltriphenylene-based polymer

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Abstract

The synthesis is reported for a main chain polymer in which the repeat units are 2,3,6,7,10,11-hexaphenyltriphenylene moieties linked through flexible dodecyl chains. In compositions with a series of 2,3,6,7,10,11-hexakis(alkoxy)triphenylenes (HATn) this new polymer forms stable hexagonal columnar liquid crystal phases. These are investigated in detail using optical polarised microscopy (OPM), differential scanning calorimetry (DSC) and X-ray diffraction (XRD). In these mixtures, suppression of crystallisation and enhancement of the clearing temperatures leads to very wide liquid crystal ranges: much wider than those for the HATn materials on their own. For the longer chain HATn compounds (n = 12-16) a columnar rectangular phase is also observed. The enhancement of the liquid crystal phase range is attributed to stabilising complementary polytopic interactions between the planar aromatic moieties.

Introduction

Although the only commercially important application of discotic liquid crystals is in the manufacture of optical compensating films (polymerised films added to liquid crystal displays which increase the angle of view) there has also been a lot of interest in their potential as self-organising/self-healing semiconductors.[1,2] In this respect complementary polytopic interaction (CPI) discotics[3-8] are particularly attractive; firstly because CPI systems have such wide mesophase ranges, and secondly because they show enhanced charge-carrier mobilities.[6] The classic example of a CPI discotic is the 1:1 mixture of 2,3,6,7,10,11-hexakis(hexyloxy)triphenylene (HAT6, Col_h phase 70-100°C, Fig. 1) with 2,3,6,7,10,11-hexakis(4'-nonylphenyl)triphenylene (PTP9, non-mesogenic, mp 58°C) where the 1:1 mixture forms a columnar phase from room temperature up to 158˚C and where it shows a hole mobility which is an order of magnitude higher than that of HAT6 on its own. In a thermodynamic sense this 1:1 mixture of HAT6 and PTP9 involves ‘compound’ formation. That is to say the 1:1 mixture represents a maximum in the temperature/composition phase diagram, it melts directly from the columnar into the isotropic phase without passing through a two-phase region and an exact equimolecular ratio of the two components is required.[3,4,7,8] If either the HAT6 or the PTP9 is present in excess it separates out. Typical examples of phase diagrams for triphenylene/hexaphenyltriphenylene CPI systems are shown in references 3,4,7 and 8. Note that these triphenylene/hexaphenyltriphenylene CPI systems are quite different to charge transfer systems such as that formed between 2,3,6,7,10,11-hexakis(pentyloxy)triphenylene (HAT5) and 2,4,7-trinitrofluorenone.[9] In the case of the HAT5/trinitrofluorenone charge transfer system various ratios of the two components can be employed, the phase diagram shows a two phase region between the columnar and isotropic phases and a charge transfer band appears when the two are mixed: they change colour. For the HAT6/PTP9 CPI ‘compound’ there is no charge transfer band: the ultraviolet spectrum of the mixture is the sum of those of the two components.

Our understanding as to why, despite the fact there is no charge transfer interaction, some triphenylene/hexaphenyltriphenylene mixtures form these stable columnar phases in which the component molecules alternate within the columns (Fig. 1), is based on extended electron distribution (XED) force field calculations[10,11] and it is because XED calculations employ dispersed, atom-centred van der Waals, quadrupolar and other coulombic terms that the term ‘Complementary Polytopic Interaction’ was coined.[3] XED calculations show that the good fit between the triphenylene and hexaphenyltriphenylene nuclei and the poor fit of the hexaphenyltriphenylene nuclei with each other are both significant factors.[12] As shown in Fig. 1, the triphenylene fits almost perfectly within the ‘bowl’-like hollow in the PTP molecule which results from the way that the peripheral phenyls of the hexaphenyltriphenylene are canted relative to the central triphenylene nucleus. In agreement with this explanation, factors which disrupt the way these molecules fit together such as α-substitution of the HAT nucleus[12,13] or planarization of the PTP nucleus[14] are found to destroy the mesophase. The poor fit of hexaphenyltriphenylene with itself is also important[10] and, in this respect, its behaviour is analogous to that of other poor self-stacking systems such as the tryptycene systems[15,16] or the spiro-fused indane polymers.[17,18] Poor molecular stacking, which is sometimes associated with high free volumes, generally leads to low lattice energies, high solubility and often easy formation of inclusion compounds. Hence the HATn/PTP systems can be viewed as an inclusion of HATn into the PTP lattice. Many variations in the structure of both the HATn and PTP components have been explored [3,12-14,19,20] including materials where the HATn component is a main chain or a side chain liquid crystal polymer.[4,21-23] However, PTP-based polymers have not yet been made.

In this paper we show that a PTP-based polymer can be synthesized and that CPI columnar liquid crystal phases are formed with a variety of HATn components but only if the HATn component is monomeric: not in the case of HAT-based polymers.

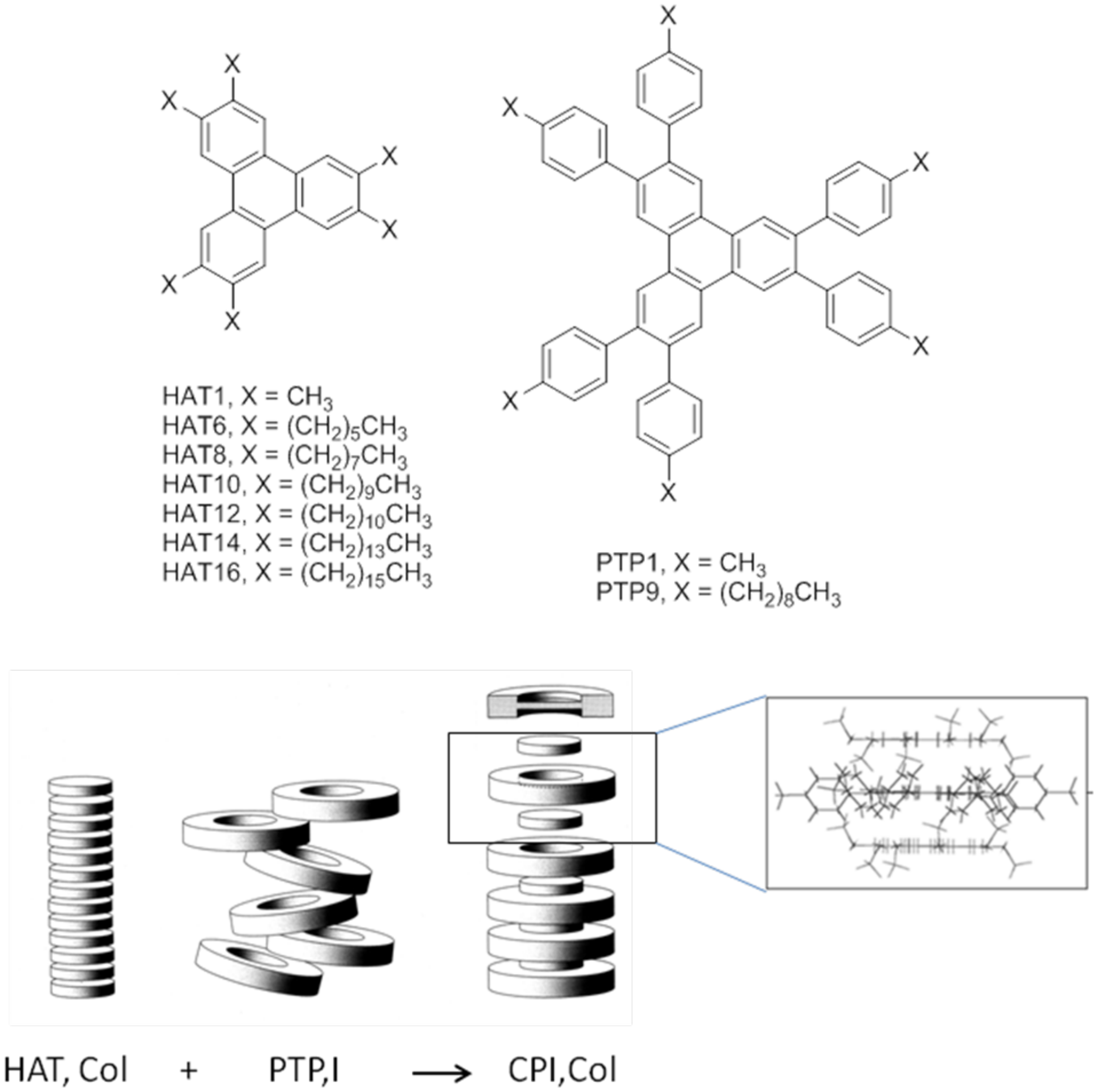


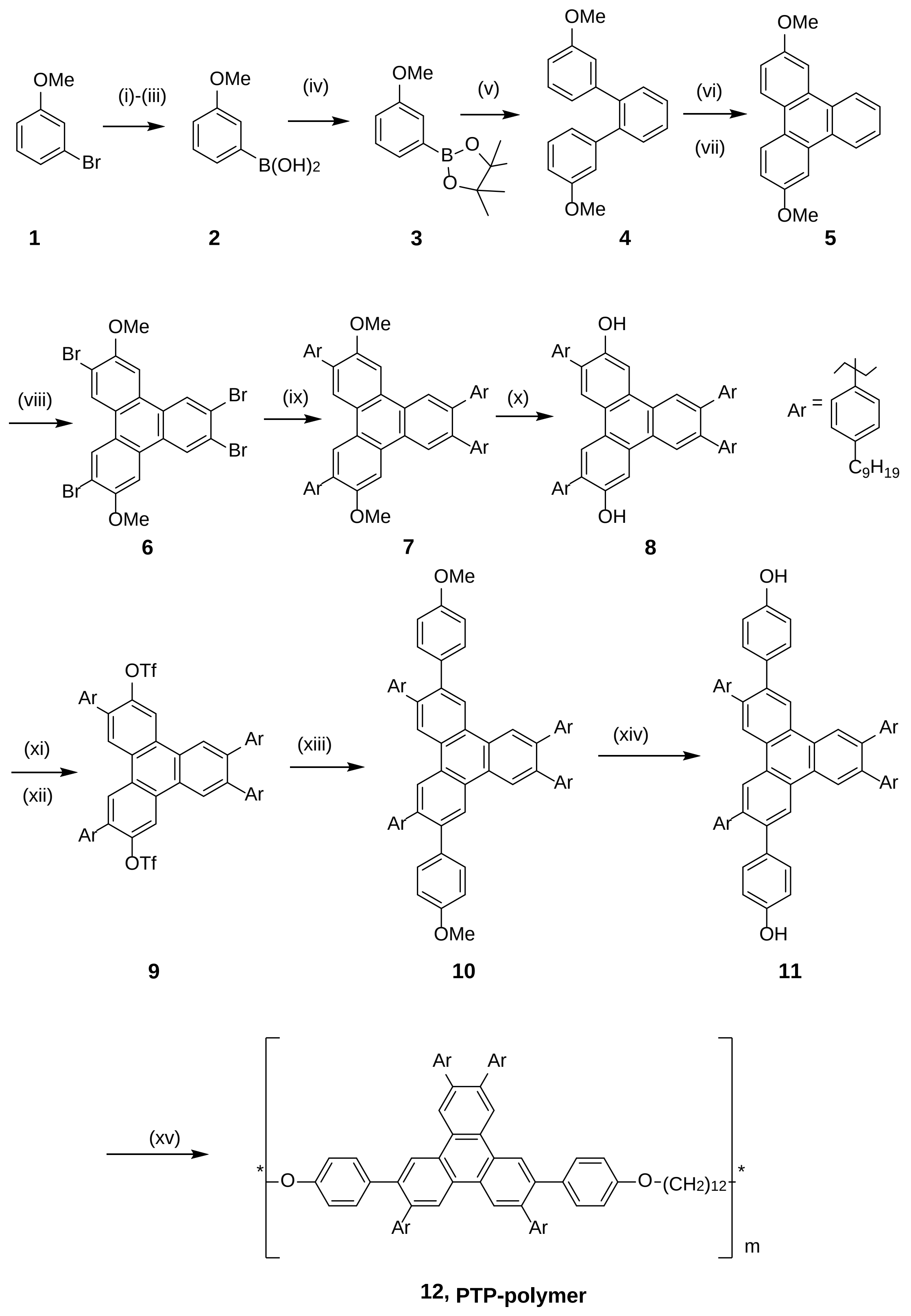
Fig. 1 Above: Formulae of the HATn and PTP molecules discussed in this paper. Below left: Schematic representation of how the HATn and PTP molecules fit together in the alternating stacks of the Col_h CPI phase. Below right: XED model of the optimum fit of one PTP1 molecule with two HAT1 molecules (side view).[10]

Results and Discussion

1. Synthesis

The synthesis of the PTP-polymer is shown in Scheme 1. 1-Bromo-3-methoxybenzene **1** was converted to the corresponding boronic acid **2** by reacting the

Grignard reagent with triisopropyl borate. On the relatively large scale required, it was found that use of the Grignard reagent was easier than using the organolithium compound although the organolithium also worked well on a small scale. Esterification of the boronic acid with pinacol,[24] followed by a Suzuki coupling[25] with 1,2-dibromobenzene gave the terphenyl **4**.[26] Treatment of this with ferric chloride in dry dichloromethane followed by an anhydrous methanolic workup[27] yielded 2,7-dimethoxytriphenylene **5**. Whist the bromination of the four available β-positions of the triphenylene ring of 2,7-hexyloxytriphenylene proceeds cleanly and in good yield under mild conditions, (Br_2, CH_2Cl_2, room temperature, 2 h),[28] this was not the case for the dimethoxy derivative **5**: partly because it is considerably less soluble in common solvents. The successful conditions for this reaction involved using refluxing tetrachloroethane as the solvent and a mixture of iron and iodine to catalyse the reaction yielding the tetrabromide **6**. A Suzuki coupling of **6** with the pinacol ester of 4-(*n*-nonyl)benzeneboronic acid[29] gave the tertaphenyltriphenylene **7** which was selectively demethylated with boron tribromide[30] and converted to the corresponding triflate **9** using triflic anhydride.[31] A further Suzuki coupling with the pinacol ester of 4-methoxy-bromobenzene[24] gave 3,6,10,11-tetra(4-nonylphenyl)-2,7-di(4-methoxyphenyl)triphenylene **10** which again was selectively demethylated with boron tribromide. Alkylation of the product **11** with 1,12-dibromododecane[21,22] gave the target PTP-polymer **12**. For all of the Suzuki couplings we used the barium hydroxide/dimethoxyethane method which has been shown to minimise competitive reduction reactions.[14]



Scheme 1. Synthesis of the polymer. Reagents: (i) Mg/THF/I_2/Δ (ii) $B(O^iPr)3$/-78 °C (iii) $HCl_{(aq)}$ (iv) Pinacol/THF/Δ (v) 1,2-Dibromobenzene/$Pd^0(PPh_3)_4$/$Ba(OH)_2$/H_2O/1,2-Dimethoxyethane/80 °C (vi)

$FeCl_3$/Dry DCM (vii) Dry MeOH (viii) Br_2/Fe^0/1,1,2,2-Tetrachloroethane/80 °C (ix) 4-*n*⁻Nonylbenzeneboronic acid pinacolate/ $Ba(OH)_2$/H_2O/1,2-Dimethoxyethane/80 °C (x) BBr_3/DCM/-78 °C – 40 °C (xi) Trifluromethanesulphonic anhydride/Pyridine/DCM/-40 °C (xii) $HCl_{(aq)}$ (xiii) 4-Methoxybenzene boronic acid pinacolate/ $Ba(OH)_2$/H_2O/1,2-Dimethoxyethane/80 °C (xiv) BBr_3/DCM/-78 °C – 40 °C (xv) 1,12-Dibromododecane/Cs_2CO_3/NMP/110 °C.

Gel Permeation Chromatography (GPC) molecular weight determination for the polymer against polystyrene standards gave $M_w = 18{,}550$ and $M_n = 9{,}700$. This indicates that, of the order of ten aromatic units are incorporated in each chain. As shown in Fig. 2, thermal differential scanning calorimetry (DSC) showed a single transition 44.5°C associated with a small enthalpy of 2.2 Jg^{-1} (Fig. 2). This transition was only observed in the first heating cycle: not on cooling or in subsequent heating cycles. Optical polarised microscopy (OPM) showed no or very weak birefringence. XRD data at room temperature showed two broad peaks, at ~ $2\theta = 3.7$ and 20.4, corresponding to distances of 23.9 Å and 4.4 Å respectively. The 4.4 Å distance is typical of alkyl-alkyl chain separation in disordered materials of this type. The value at 23.9 Å distance is less easy to understand but it may correspond to the separation between aryl moieties in adjacent polymer chains. Taken together it seems that the polymer is largely amorphous, but that the ‘as synthesised’ material may containing a small proportion of a crystalline component which does not reform once the polymer has been melted. The absence of any mesoscopic register is not surprising as the linking in the main chain polymer results in a structural motif which is quite non-symmetric (if the polymerisation link is considered as a symmetry axis for the aromatic groups). Moreover the dodecyl hydrocarbon link is quite short when compared to the aromatic part of the polymer which contains four *para*-nonyl substituted phenyl groups.

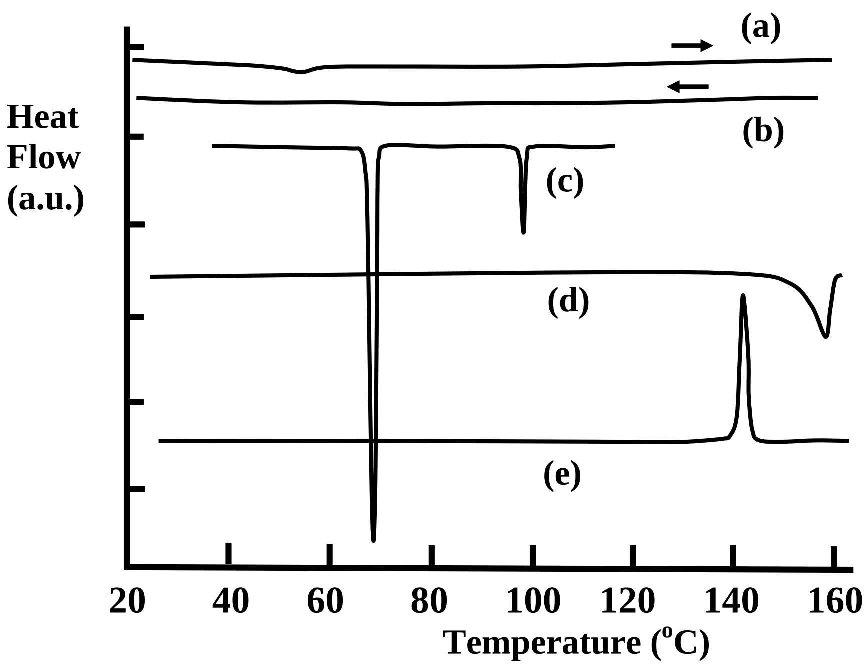


Fig. 2. DSC data discussed in the text. (a) PTP-polymer **12** first heating. The very weak broad endotherm, onset 44.5°C, is not seen in the second and third heating runs. (In all of these traces endotherm peaks are negative) (b) PTP-polymer **12** first cooling. (c) HAT6 first heating. This is reproducible over many heating/cooling cycles. (d) 1:1 mixture of the PTP-polymer **12** with HAT6 first heating. (e) 1:1 mixture of the PTP-polymer **12** with HAT6 first cooling. The traces for the CPI 1:1 mixture of the PTP-polymer **12** with HAT6 are reproducible over at least three cycles. Note that the clearing temperature of the CPI mixture is higher than that for either of the two components measured individually.

~~<<Fig. 2>>~~

2. Characterisation of the CPI mixtures

The DSC of a 1:1 mixture of the polymer and HAT6 (1:1 in terms of HAT6 *versus* the repeat unit of the polymer) shows a single phase transition at 151°C (ΔH, 16 Jg^{-1}) and this transition is reversible although there some supercooling was observed in the cooling cycle (Fig. 2). These transitions were reproducible over many heating and cooling scans. As is usual for CPI mixtures, the clearing temperature of the 1:1 mixture is significantly higher (151.3 °C) than that of either of the pure PTP-polymer at 44^{o}C or of HAT6 at 100^{o}C (Fig. 2). OPM defect textures collected for samples of the mixture sandwiched between untreated glass slides show a clear mosaic texture (Fig. 3). This observation is surprising because such textures are normally associated with the Col$_h$ phase of low molar mass discogens. It is quite unlike the sandy texture, made up of many tiny domains, which are usually observed for Col$_h$ phases of discotic liquid crystal polymers.[23] As with CPI-based polymers previously studied it seems that unusually large and ordered domains are formed.[13]

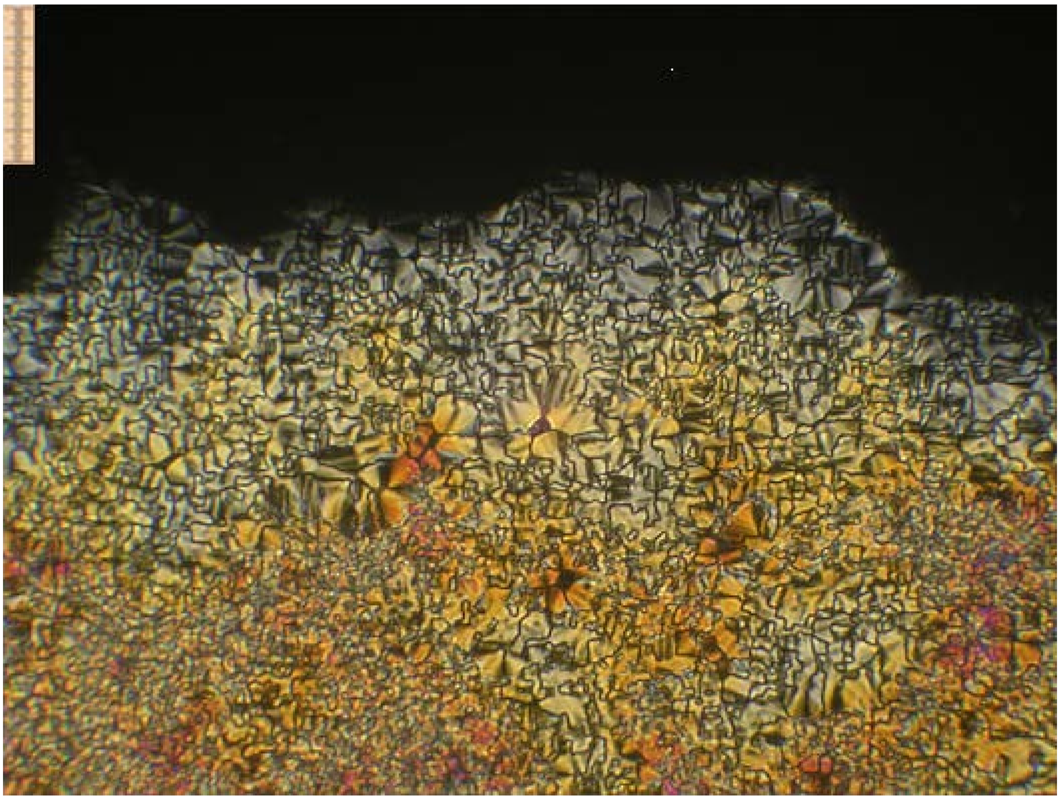


Fig. 3.– 1:1 Mixture of the polymer with HAT6 as it appears through crossed optically polarized filters at 110°C, (cooled from 175°C to 14°C at 0.1°Cmin^{-1} and from 140°C to 110°C at 0.5°Cmin^{-1}). Scale bar = 100 µm.

XRD data for a sample at 50^{o}C (Fig. 4) showed the mixed phase to be Col$_h$ (100 reflection at 21.5 Å; 110 at 12.4 Å; 001 at 3.50 Å; broad chain/chain reflection at ~4.2 Å). There was small increase in the values for the lattice when the temperature was raised to 150^{o}C but no indication of significant decrease in positional ordering, since the width of the peak for the main small angle reflection did not vary by much.

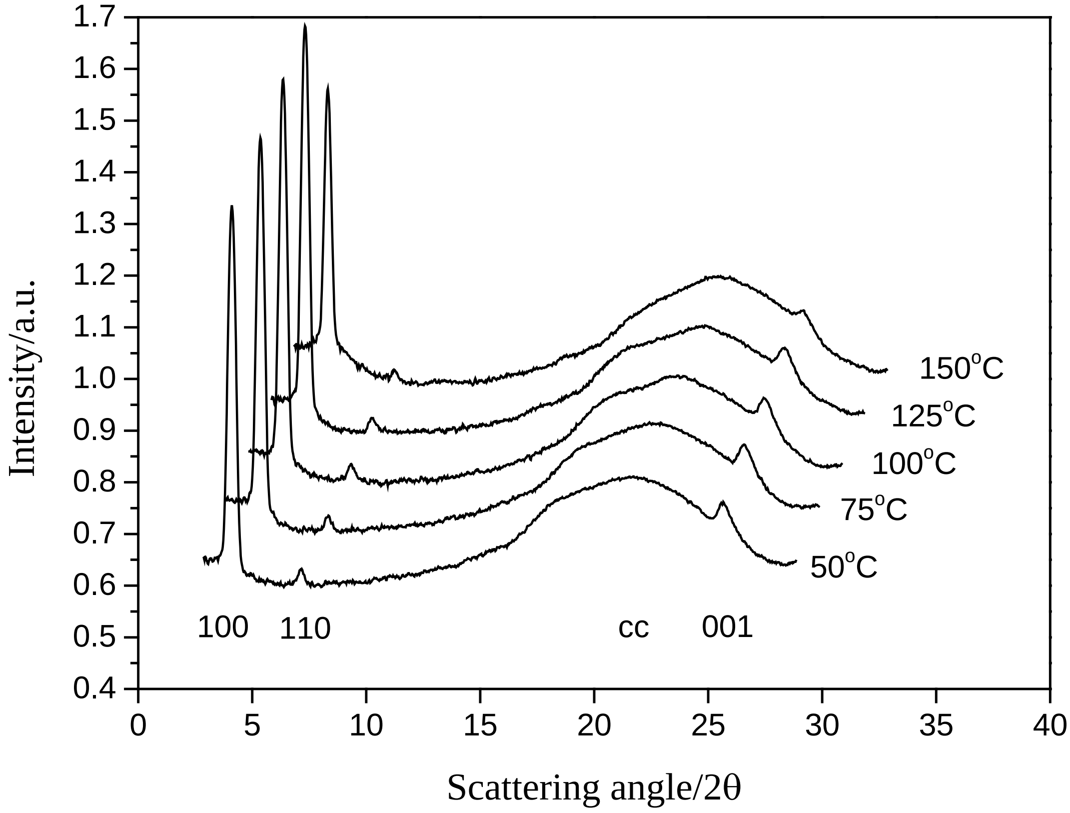


Fig. 4. XRD data (2θ *vs.* intensity (arbitrary units)) for the 1:1 mixture of the polymer and HAT6 between 50 and 150°C. The data for 75-150°C is shown displaced.

Similar behaviour was also found for 1:1 mixtures of the polymer with HAT8, HAT10, HAT12, HAT14 and HAT16[32] except, that the OPM defect textures, for these longer side-chain systems, showed a more spherulitic like texture as shown for the HAT8 mixture depicted in Fig. 5a which has unusually large organised domain structures. Most probably the phase is aligned in a planar manner with each ‘Maltese Cross’ corresponding to a developable domain viewed along the line of an S=1 disclination.[33-35]

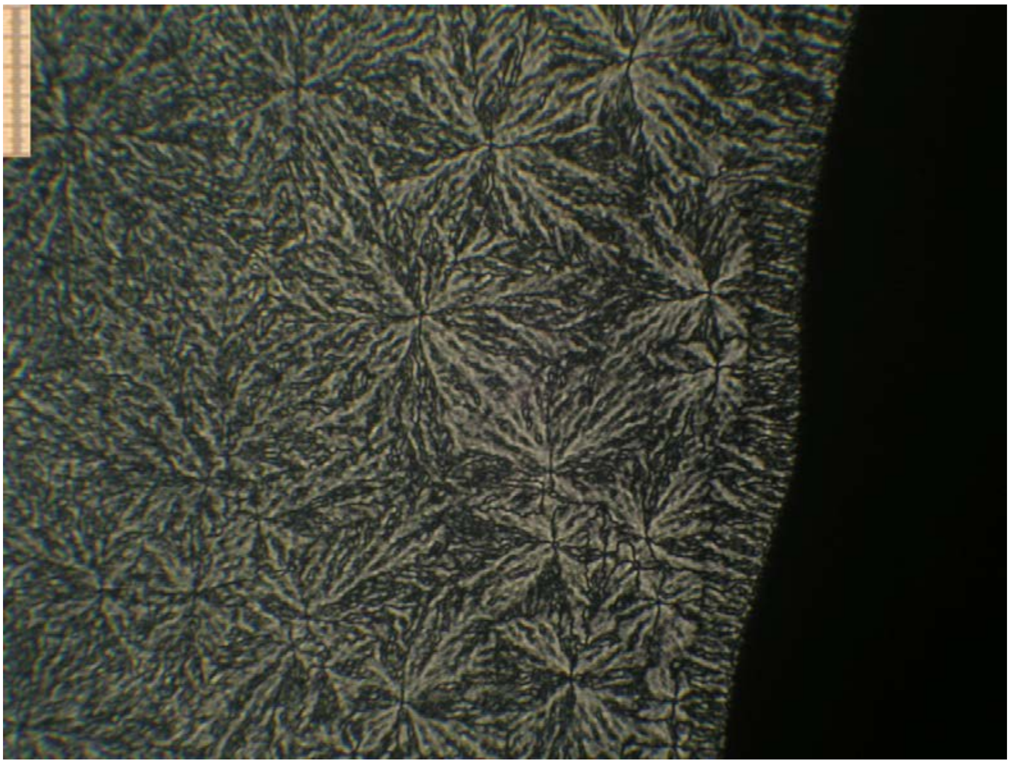


Fig. 5a. POM for a 1:1 mixture of the polymer with HAT8 at 120°C as it appears through crossed optically polarized filters (recorded at x100 magnification). Cooled from the isotropic melt at 0.5°C min^{-1}. Scale bar = 100 µm.

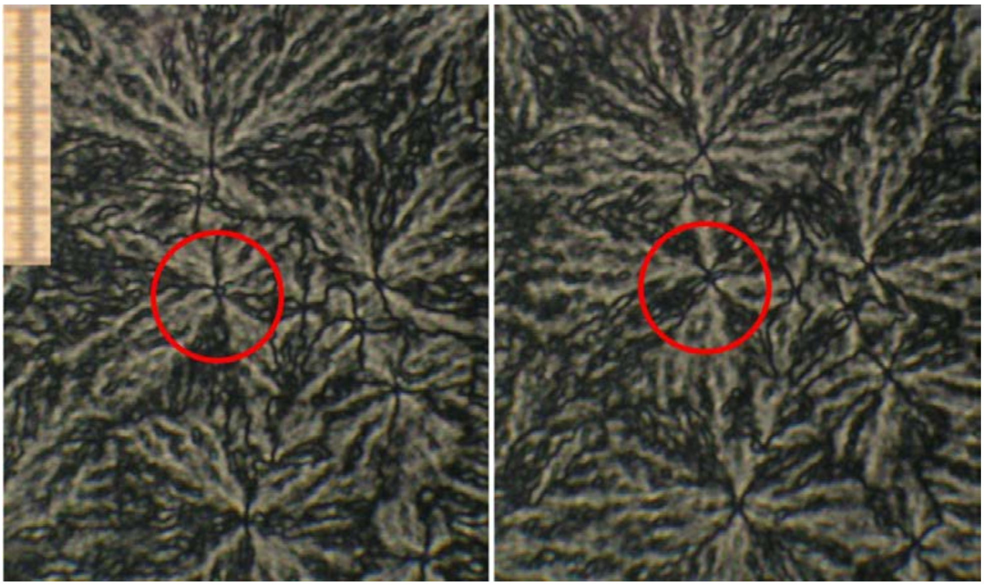
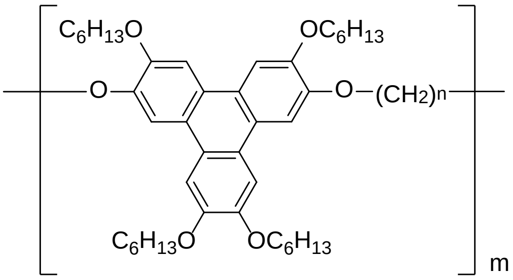


Figure 5b. Detail from Fig. 5a showing the rotation of the ‘brush-like’ features (circled in red), with the rotation of the crossed polarising filters. In the right hand image the polarising filters are both rotated by 45°. Scale bar = 100 μm

The results of the DSC studies for HATn components with different chain lengths are summarised in Table 1 and the data is presented in graphical form in Fig. 6.

Just as the melting point of the polymer (44.5^{o}C) and that of PTP9 (58^{o}C) are quite close to each other so also the clearing points of the 1:1 mixtures of the polymer with various HATn derivatives and the clearing points of the 1:1 mixtures of PTP9 itself with these HATn derivatives closely follow the same line. (Compare the red and black lines in Fig. 6). In terms of the basic phase behaviour it is apparent that linking the side chains of the PTP together to generate a main chain polymer does not alter the liquid crystal transitions significantly. The 1:1 mixed mesophase is much more stable than the mesophase formed by HATn on its own (Fig. 6, blue lines). Also note that whereas on their own HAT14 and HAT16 do not form a mesophase, when they are mixed with the PTP-polymer, both $\mathrm{Col_h}$ and $\mathrm{Col_r}$ mesophases are observed.

It is also interesting to compare this data with that for systems in which the PTP component is low molar mass but the HAT component is polymeric. Hence, mixtures of PTP9 with the polymers **13a-c** (Scheme 2) give CPI columnar hexagonal phases with clearing temperatures of 100, 128 and 156^{o}C respectively.[5] This trend in clearing temperatures may relate to the length of the polymethylene chain. A hexadecylmethylene chain (**13c**) can easily bridge between two columns in the columnar phase and in the case of **13c**/PTP9 the phase behaviour is remarkably similar to that for the equivalent low molar mass (HAT6:PTP9) mixture but for the undecyl and octyl linkers (**13a**, **13b**) this is less easy and, as a result, the mesophase range is more restricted.



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Scheme 2. Main-chain polymers based on a repeating HATn moiety. **13a**, n=8; **13b**, n=11; **13c**, n=16 (see text).

Molecule	1:1 Mixture with	Phase Behaviour Temperature ^{o}C (Enthalpy J g^{-1})
PTP-polymer	-	amorphous? 44.5 (2.2) I
PTP-polymer	HAT6	Col_h 151.3 (16.1) I
PTP-polymer	HAT8	Col_h 172.4 (13.8) I
PTP-polymer	HAT10	Col_r 71.3 (2.4) Col_h 163.5 (7.5) I
PTP-polymer	HAT12	Col_r 66.9 (4.2) Col_h 169.4 (8.3) I
PTP-polymer	HAT14	Col_r 40.2 (1.0) Col_h 167.4 (14.4) I
PTP-polymer	HAT16	Col_r 47.1 (3.4) Col_h 151.2 (13.7) I

Table 1. Phase behaviour for 1:1 mixtures of the PTP-polymer and HATn compounds. Peak onset temperatures ^{o}C (Enthalpy J g^{-1})

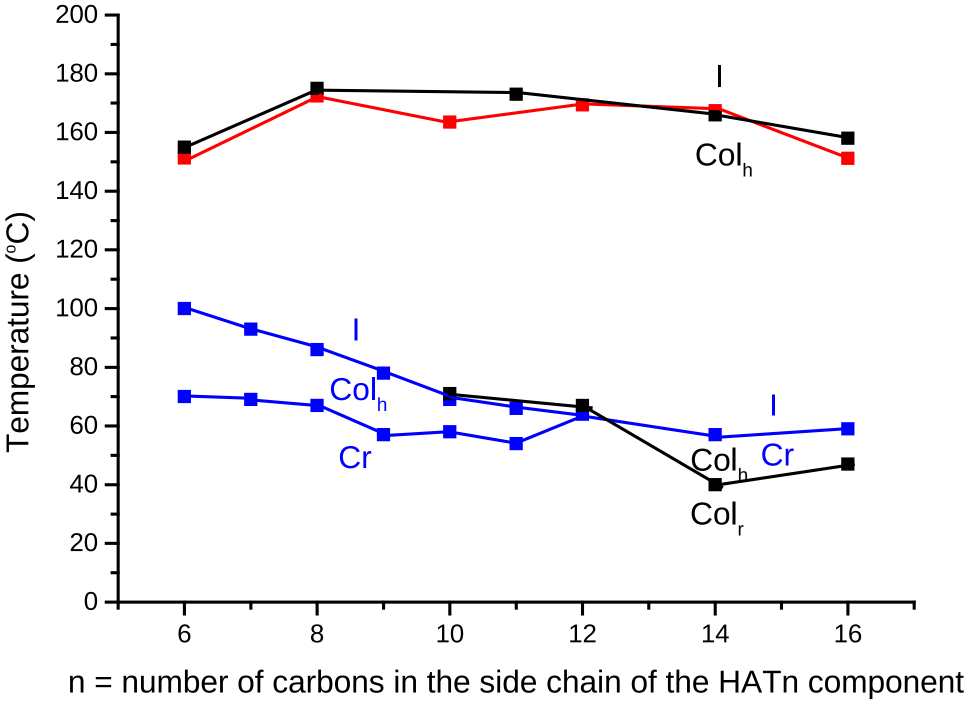

Fig. 6 Phase transitions for 1:1 HATn:PTP-polymer (black lines) and for 1:1 HATn:PTP9 (red line) mixtures and those for for HATn (blue lines). The labels in blue refer to the phases formed by the HATn materials on their own and those in black to the 1:1 mixtures.

The XRD data for the mixtures of the PTP-polymer with HATn is summarised in Table 2. The way the cell dimensions vary with the chain length is broadly in line with data for similar low molar mass systems as is the way the unit cell dimensions increase on raising the temperature. This is associated with an increase of the mobility of the aliphatic chains and a decrease in the density. As well as the expected Col$_h$ phase, the mixtures with HAT10, HAT12 and HAT16 all show a Col$_r$ (columnar rectangular) liquid crystalline phases at lower temperatures. Although it has not been investigated fully it is known that, as well as the Col$_h$ phase, a 'more ordered phase' is formed at lower temperatures by mixtures of PTP9 with HAT8, HAT11, HAT14 and HAT16.[36] This 'more ordered phase' had (tentatively) been identified as 'crystalline' but, in view of the present findings, it seems probable that this was also a Col$_r$ phase.

Sample	Phase	Temp (°C)	100	010	110	200	210	020	300	cc	001
PTP-polymer	amorphous	20	23.9							4.4	
PTP-polymer:HAT6	$\mathrm{Col_h}$	50	21.5		12.4					4.2	3.5
PTP-polymer:HAT6	$\mathrm{Col_h}$	150	21.9		12.7					4.2	3.6
PTP-polymer:HAT8	$\mathrm{Col_h}$	25	22.3		12.9	11.1	8.4			4.5	3.5
PTP-polymer:HAT8	$\mathrm{Col_h}$	110	22.7		13.1	11.3	8.6			4.5	3.5
PTP-polymer:HAT10	$\mathrm{Col_r}$	25	31.8	23.2			13.4	11.6	10.6	4.2	3.5
PTP-polymer:HAT10	$\mathrm{Col_r}$	40	32.3	23.7			13.6	11.9		4.2	3.4
PTP-polymer:HAT10	$\mathrm{Col_h}$	70	23.8		13.7	11.9				4.2	3.4
PTP-polymer:HAT10	$\mathrm{Col_h}$	160	23.9							4.2	3.4
PTP-polymer:HAT12	$\mathrm{Col_r}$	25	37.0	24.1			13.9	12.1		4.5	3.5
PTP-polymer:HAT12	$\mathrm{Col_r}$	40	36.8	24.2			14	12.1		4.5	3.5
PTP-polymer:HAT12	$\mathrm{Col_h}$	70	24.2		14.0	12.1	9.2			4.5	3.5
PTP-polymer:HAT12	$\mathrm{Col_h}$	160	24.7		14.3	12.4	9.3			4.5	3.5
PTP-polymer:HAT16	$\mathrm{Col_r}$	30	44.3	25.5				12.7	14.8	4.1	3.4
PTP-polymer:HAT16	$\mathrm{Col_h}$	60	25.8		14.9	12.9				4.1	3.4
PTP-polymer:HAT16	$\mathrm{Col_h}$	160	26		15.0	13.0				4.1	3.4

Table 2. Indexed X-Ray reflections d-spacings (Å) for the 1:1 mixtures of the polymer with the HATn discotics. The label c.c represents the separation between the fluid/disordered alkyl side chains. This reflection is very broad. (see Fig. 4).

It has now been shown that in HAT/PTP CPI mixtures either the HAT or PTP component can be polymeric. The question then arises as to whether *both* components can be polymeric: whether the interaction between the HAT and PTP moieties is sufficiently strong to drive the intimate mixing of polymers. However, when the PTP-polymer was mixed 1:1 (in terms of the repeat units) with a selection of the main-chain and side-chain HAT polymers and HAT-based block-copolymers[21-23] and the solutions were then evaporated we failed to produce a stabilised mesophase. Rather phase-separation occurred. Hence, for example, a 1:1 mixture of PTP-polymer with the main chain HAT polymer **13b** on evaporation and subsequent investigation by DSC showed no phase transitions below 200°C other than were very weak peaks at 4

6°C (~the melting point of the PTP-polymer) and at 117°C (~the Col_h-I transition of compound **13b**[4]).

Conclusions

Previous work had shown that formation of CPI columnar phases is possible using a wide range of different HATn and PTP components[3,12-14,19,20] and that the HATn component could be a main-chain or a side-chain liquid crystal polymer.[5] In this paper we show that the PTP component can also be a main-chain polymer but only if the HATn component is low molar mass: not if it is polymeric. The columnar LC phases formed are all stable down to room temperature and they do not crystallise. Since they also have higher clearing temperatures than the HATn components on their own they are stable over much wider temperature ranges. Higher ordered columnar rectangular phases are detected for mixtures of long chain HATn molecules with the polmer (n =10-16) and these are potentially particularly interesting since they should show particularly high hole mobilities.[6] The spontaneous formation of large domains in these mixture is quite unlike the behaviour of typical main-chain discotic LC polymers. Hence, using CPI PTP-polymer mixtures provides a route to highly ordered columnar phases which spontaneously form large aligned domains. Like other HATn/PTP CPI mixtures, these are potentially interesting as self-organising/self-healing semiconductors.[1,2]

Experimental Section

1. General Methods

Unless otherwise stated, all reagents and solvents were obtained from commercial suppliers and used without further purification. Anhydrous solvents were used as supplied (water content < 0.05%). Flame dried refers to glassware that was flame dried under vacuum (≈0.05 mbar) for *ca.* 10 min and subsequently purged with argon using double manifold apparatus. ^{1}H and ^{13}C{^{1}H} spectra were recorded on a Bruker 400 MHz or 500 MHz spectrometer. The progress of reactions was monitored by TLC on pre-coated silica plates visualized by ultraviolet light or staining with vanillin or potassium permanganate in the absence of a chromophore. Column chromatography employed Merck Kieselgel (60 Å) F_{254} (230–400 mesh) silica and HPLC grade solvents. Compounds were recrystalised to a constant melting point. Polarizing optical microscopy images were captured on an Olympus BH2 polarizing optical microscope equipped with a digital camera and the sample temperature controlled by a Linkam LTSE350 heating stage. Differential scanning calorimetry used a Perkin-Elmer DSC 7 with 1.5-3 mg samples in closed Al pans. Heating and cooling scans were at 10 °Cmin^{-1}. Peak onset values (°C) are reported with the associated transition enthalpies (ΔH) in Jg^{-1}. Microanalyses were performed by the Analytical Chemistry Service at the University of Leeds and the GPC molecular weight measurements by Rapra technology, Shawbury, UK.

2. X-ray diffraction experiments

X-ray diffraction experiments were performed at room temperature and for compounds exhibiting mesomorphism, at a range of temperatures increasing towards the transition temperature from the liquid crystalline to isotropic phase. Diffraction patterns were collected, using a MAR345 X-ray research detector and Seifert X-ray generator with wavelength λ=0.154 nm. Samples were typically packed into Lindemann sample tubes with an internal diameter of 0.9 mm. Exposure times of 600 and 1200 s were used to collect diffraction patterns. A number of SAXS x-ray diffraction experiments were also performed at the Daresbury Synchrotron Radiation Source.

Powder samples were packed into glass capillary tubes, degassed under argon and flame sealed. Where samples were of a sticky nature the material was introduced into the mouth of a capillary tube, there forming a plug. The loaded tube was then placed into a hot aluminium block and centrifuged until the material was packed at the bottom of the tube without visible air bubbles prior to flame sealing. Plots of intensity *vs.* 2θ were produced using the ‘fit2D’ software package for UNIX. Peaks were indexed and unit cells refined using the ‘PowderX’ software package incorporating a visual basic cell refining routine written by Cheng Dong, and based upon the ‘Celref’ routine, (originally written by J. Laugier and A. Filhol, 1978). Lattice distances were calculated with a spreadsheet to within ±0.3 Å. The package ‘Powder’, coded by T. C. Gibb, Department of Chemistry, University of Leeds, was used to aid assignment of the unit cell parameters.

3. Synthesis

Compound 4: 3,3’’-Dimethoxy[1,1’;2,’1’’]terphenyl

3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-methoxy benzene (28.61 g, 122 mmol) and 1,2-dibromobenzene (15.1 g, 55.6 mmol) dissolved in 1,2-dimethoxyethane (350 mL) and water (5 mL) was degassed with argon for 1 h. Under a fast stream of argon, tetrakis(triphenylphosphine)palladium(0) was added and the mixture degassed for a further 0.5 h, followed by addition of barium hydroxide octahydrate (38.5 g, 122 mmol). The reaction was brought to 80°C for 48 h. The reaction mixture was allowed to cool to room temperature and diluted with DCM (100 mL). The solution was filtered through a silica/celite plug (eluting with DCM). The filtrate was concentrated *in vacuo* to afford a pale yellow oil, which crystallised on standing to afford the title compound (12.05 g, 34%). mp 89-90°C (EtOH, Lit 89-91°C[26]). **^{1}H NMR** (400 MHz, CDCl$_3$, δ): 7.54 – 7.38 (m, 4H), 7.14 (t, *J* = 6.88 Hz, 2H), 6.89 – 6.84 (m, 4H), 6.67 – 6.64 (m, 2H), 3.85 (s, 6H). **^{13}C NMR** (100 MHz, CDCl$_3$, δ): 159.06, 142.87, 140. 42, 130.40, 128.88, 127.55, 122.28, 115.09, 112.65, 55.11; HRMS (EI$^+$, 70 eV); *m/z* $[M]^+$ calcd for $C_{20}H_{18}O_2$ 290.1307, found 290.1296. IR (ATR) $\bar{\nu}_{max}$ (cm^{-1}); 3086, 31013, 2960, 2933, 2837, 1604, 1592, 1580, 1474; Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25%; Found: C, 82.48; H, 6.28%.

Compound 5: 2,7-Dimethoxytriphenylene

Ferric chloride (14.8 g, 91.3 mmol, 2.2 eq) was added portionwise to a cooled (0°C) solution of 3,3”-dimethoxy-[1,1’,2’,1”]terphenyl (12.05 g, 41.5 mmol) dissolved in anhydrous DCM (300 mL) protected with a calcium chloride guard tube. Upon completion of the addition, the mixture turned to a deep blue and stirring was continued for 18 h at room temperature. With cooling (0°C) methanol (200 mL) was carefully added to quench to mixture. The resultant mixture was diluted with DCM (300 mL), washed successively with 1 M HCl (2 × 200 mL), water (2 × 200 mL), dried ($MgSO_4$) and concentrated *in vacuo*. The crude was filtered through a celite/silica plug (eluting with DCM) to afford the title compound as fine colourless needles (7.68 g, 64%). mp 156 – 157°C (EtOH, Lit 153-155 ºC[26]). **^{1}H NMR** (CDCl$_3$, 400 MHz, δ): 8.61 (dd, *J* = 6.24 & 2.88 Hz, 2H), 8.50 (d, *J* = 9.04 Hz, 2H), 8.06 (d, *J*

= 2.60 Hz, 2H), 7.67 (dd, *J* = 6.24 & 3.32 Hz, 2H), 7.30 (dd, *J* = 8.64 & 2.60 Hz), 4.05 (s, 6H); **^{13}C NMR** ($CDCl_3$, 100 MHz, δ): 158.22, 130.13, 129.92, 127.17, 124.39, 123.98, 123.42, 115.96, 105.76, 55.51; HRMS (EI^+, 70 eV); *m/z* $[M]^+$ calcd for $C_{20}H_{16}O_2$ 288.1150, found 288.1139. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}); 2962, 2939, 2909, 2839, 1612, 1498, 1452, 1428; Anal. Calcd for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59%; Found: C, 83.02; H, 5.52%.

Compound 6: 3,6,10,11-Tetrabromo-2,7-dimethoxytriphenylene

Bromine (2.51 mL, 50.0 mol) was added to a stirred mixture of 2,7-dimethoxytriphenyle (2.88 g, 10 mmol), iron powder (*cat*. amount), iodine (*cat*. amount) stirred in tetrachloroethylene (1000 mL). The mixture was stirred at reflux for 24 h before heating to reflux for 7 h. The reaction was cooled to room temperature and sodium metabisulphite (*sat*. ~ 200 mL) was added until decolourisation was complete. The solids were removed by filtration and washed with water (200 mL), ethanol (200 mL) and diethyl ether (200 mL) prior to drying *in vacuo*. The white solids were dissolved in boiling tetrachloroethylene and filtered hot. The filtrate was allowed to cool and the solids collected by filtration to afford the title compound as fine white needles (4.16 g, 69%). mp 325-327°C decomp. (o-dichlorobenzene). **^{1}H NMR** (500 MHz, $CDCl_2CDCl_2$, 80°C, δ): 8.74 (s, 2H), 8.60 (s, 2H), 7.82 (s, 2H), 4.16 (s, 6H); **^{13}C NMR** (125 MHz, $CDCl_2CDCl_2$, 80°C, δ): 155.11, 129.63, 128.12, 127.96, 127.65, 123.99, 123.95, 114.62, 104.89, 56.71; HRMS (EI^+, 70 eV); *m/z* $[M]^+$ calcd for $C_{20}H_{12}O_2{}^{79}Br_2{}^{81}Br_2$ 603.7530, found 603.7519. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}); 2960, 2918, 2850, 1605, 1479, 1465, 1402 Anal. Calcd for $C_{20}H_{12}O_2Br_4$: C, 39.78; H, 2.00; Br, 52.92%; Found: C, C, 39.75; H, 2.00; Br, 52.70%.

Compound 7: 2,7-dimethoxy-3,6,10,11-tetra(4-*n*-nonylphenyl)triphenylene

3,6,10,11-tetrabromo-2,7-dimethoxytriphenylene (1.90 g, 3.15 mmol), 4-*n*-nonylbenzeneboronic acid pinacolate (4.99 g, 15.10 mmol, 4.8 eq) were dissolved in a mixture of 1,2-dimethoxyethane (300 mL) and water (6 mL). The mixture was degassed with argon for 1 h and charged with tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol, 8 mol %) and barium hydroxide octahydrate (4.96 g, 15.75 mmol, 5 eq) and the mixture was degassed for a further 0.5 h and brought to 80°C for 96 h. The reaction mixture was allowed to cool and filtered through a celite/silica plug (eluting with DCM). The filtrate was washed successively with water (3 × 200 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the crude product as a brown amorphous solid. The title compound was purified by column chromatography cyclohexane to 25% DCM:cyclohexane (Rf ≈ 0.45) to afford the title compound as a sticky amorphous solid (3.12 g, 90%). **^{1}H NMR** ($CDCl_3$, 400 MHz, δ): 8.62 (s, 2H), 8.52 (s, 2H), 8.12 (s, 2H), 7.63 (d, *J* = 8.04 Hz, 4H), 7.32 (d, *J* = 8.04 Hz, 4H), 7.28 (d, *J* = 8.04 Hz, 4H), 7.15 (d, *J* = 8.04 Hz, 4H), 4.05 (s, 6H), 2.72 – 2.64 (m, 8H), 1.73 – 1.65 (m, 8H), 1.42 - 1.20 (m, 48H), 0.92 (t, *J* = 6.65 Hz, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz, δ): 155.66, 142.12, 141.45, 139.70, 139.00, 135.72, 131.54, 130.00, 129.65, 129.10, 128.84, 128.23, 128.06, 127.40, 125.63, 125.31, 124.04, 104.00, 55.90, 35.83, 35.67, 31.95, 31.94, 31.54, 31.47, 29.66, 29.61, 29.51, 29.40, 22.72, 13.17; HRMS (APCI); *m/z* $[M+H]^+$ calcd for $C_{80}H_{105}O_2$ 1097.8109, found 1097.8107. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}) 2923, 2853, 1608, 1512, 1482, 1464; Anal. Calcd for $C_{80}H_{104}O_2$: C, 87.54; H, 9.55%; Found: C, 87.40; H, 9.65%.

Compound 8: 2,7-dihydroxy-3,6,10,11-tetra(4-*n*-nonylphenyl)triphenylene

To a flame dried flask under an argon atmosphere was charged 2,7-dimethoxy-3,6-10,11-tetra(4-*n*-nonylphenyl)triphenylene (0.96 g, 0.875 mmol) and anhydrous DCM (10 mL). The mixture was cooled to -78°C and BBr_3 (0.35 mL, 0.35 mmol, 1.0 M in DCM) was added dropwise. The reaction was allowed to warm to room temperature overnight and quenched with the addition of water (~5 mL). The mixture was extracted with DCM (3 × 50 mL), the combined organics washed successively with water (2 × 30 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the crude title compound which was purified by column chromatography eluting 10% DCM/cyclohexane to 30% DCM/cyclohexane (Rf ≈ 0.40) to afford the title compound as a colourless sticky amorphous solid (0.80 g, 85%). **^{1}H NMR** ($CDCl_3$, 400 MHz, δ): 8.58 (s, 2H), 8.40 (s, 2H), 8.21 (s, 2H), 8.55 (d, *J* = 8.04 Hz, 4H). 7.38 (d, *J* = 8.04 Hz, 4H), 7.26 (d, *J* = 8.04 Hz, 4H), 7.15 (d, *J* = 8.04 H), 5.43 (s, br, 2H), 2.73 – 2.69 (m, 4H), 2.66 – 2.62 8m, 4H), 1.70 – 1.62 (m, 8H), 1.38 – 1.20 (m, 48H), 0.92 (t, *J* = 6.65 Hz, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz, δ): 151.49, 143.21, 141.36, 138.81, 134.16, 130.02, 129.88, 129.50, 129.14, 129.04, 128.59, 128.05, 125.77, 124.87, 124.11, 108.79, 25.77, 35.66, 31.95, 31.54, 31.43, 29.66, 29.59, 29.56, 29.40, 29.37, 29.34, 22.73, 22.71, 14.16; HRMS (FAB$^+$) *m/z* [M+H]$^+$ calcd for $C_{78}H_{101}O_2$ 1069.7796, found 1069.7807. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}) 3365 (b), 2925, 2921, 2854, 1622, 1512, 1485, 1465, 1427; Anal. Calcd for $C_{78}H_{100}O_2$: C, 87.58; H, 9.42%; Found: C, 87.30; H, 9.60%.

Compound 9: 2,7-di(trifluoromethanesuphonato)-3,6-10,11-tetra(4-*n*-nonylphenyl)triphenylene

To a flame dried flask under and argon atmosphere was charged anhydrous DCM (40 mL),2,7-dihydroxy-3,6,10,11-tetra(4-*n*-nonylphenyl)triphenylene (0.82 g, 0.765 mmol) and pyridine (0.51 mL, 6.3 mmol). The reaction was cooled to -40°C and trifluoromethanesulphonic anhydride (2 mL, 11.8 mmol) was added dropwise. The reaction was allowed to warm to room temperature overnight and 1 M HCl (15 mL) was added. The reaction mixture was extracted with DCM (3 × 50 mL), the combined organics washed successively with 1 M HCl (2 × 20 mL), water (2 × 20 mL), brine (2 × 20 mL), dried (MgSO4) and concentrated *in vacuo* to afford the title compound as colourless fine needles (0.90 g, 88%). mp (118-120°C, EtOH/$CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$, δ): 8.70 (s, 2H), 8.65 (s, 2H), 8.57 (s, 2H), 7.57 (d, *J* = 7.96 Hz, 4H), 7.38 (d, *J* = 7.92 Hz, 4H), 7.27 (d, *J* = 7.96 Hz, 4H), 7.17 (d, *J* = 7.96 Hz, 4H), 2.75 – 2.71 (m, 4H), 2.70 – 2.66 (m, 4H), 1.72 – 1.60 (m, 8H), 1.39 – 1.20 (m, 48H), 0.95 – 0.92 (m, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz, δ): 146.84, 143.71, 141.98, 141.59, 138.06, 134.62, 132.70, 130.60, 129.82, 129.50, 128.77, 128.27, 127.92, 127.37, 125.54, 120.02, 116.96, 116.3, 35.76, 35.68, 31.95, 91.92, 31.46, 29.65, 29.59, 29.55, 29.40, 29.35, 29.26, 22.73, 22.70, 14.15; HRMS (FAB+); *m/z* [M+H]$^+$ calcd for $C_{80}H_{99}F_6O_6S_2$ 1333.6782, found 1333.6811. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}) 3028, 2924, 2855, 1512, 1417. Anal. Calcd for $C_{80}H_{98}F_6O_6S_2$: C, 71.08; H, 7.46%; Found: C, 71.15; H, 7.40%.

Compound 10: 2,7-di(4-methoxyphenyl)-3,6,10,11-tetra(4-*n*-nonylphenyl)triphenylene

Distilled water (1 mL), 2,7-di(trifluoromethanesuphonato)-3,6-10,11-tetra(4-*n*-nonylphenyl)triphenylene (0.746 g, 0.559 mmol) and 4-methoxyphenylboronic acid, pinacol ester (0.310 g, 1.34 mmol) were added to 1,2-dimethoxyethane (50 mL) under and argon atmosphere. The mixture was degassed for 1 h with stirring, barium hydroxide octahydrate (0.44 g, 1.4 mmol) and tetrakis(triphenylphosphine)palladium(0) (26 mg, 0.025 mmol, 4 mol %) was added under a fast stream of argon. The reaction mixture was degassed for a further 0.5 h and brought to 80°C for 96 h. The reaction was allowed to cool to room temperature and filtered over a celite/silica pad eluting with DCM. The filtrate was washed successively with water (3 × 50 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the crude title compound which was purified by column chromatography eluting 20% DCM/cyclohexane (Rf ≈ 0.35) to afford the title compound as a colourless glassy material. **^{1}H NMR** ($CDCl_3$, 400 MHz, δ): 8.73 (s, 2H), 8.72 (s, 2H), 8.71 (s, 2H), 7.31 - 7.26 (m, 3 × unresolved doublets, 12H), 7.17 (d, *J* = 6.88 Hz, 4H), 7.15 (d, *J* = 7.76 Hz, 4H), 6.87 (d, *J* = 6.87 Hz), 3.87 (s, 6H), 2.66 (t, *J* = 7.52 Hz, 8H), 1.69 – 1.60 (m, 8H), 1.38 – 1.20 (m, 48H), 0.93 (t, *J* = 6.52 Hz, 12H); **^{13}C NMR** ($CDCl_3$, 100 MHz, δ): 158.50, 141.41, 141.39, 139.87, 139.84, 139.41, 138.92, 138.89, 134.09, 131.20, 129.95, 128.85, 128.82, 128.73, 128.11, 128.03, 125.56, 125.49, 125.38, 113.45, 55.25, 35.67, 31.95, 31.45, 29.65, 29.63, 29.60, 29.58, 29.40, 29.37, 22.73, 14.17; HRMS (FAB+); *m/z* $[M+H]^+$ calcd for $C_{92}H_{113}O_2$ 1249.8735, found 1249.8747. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}): 2956, 2924, 2854, 1446, 1417; Anal. Calcd for $C_{92}H_{113}O_2$: C, 88.33; H, 9.10%; Found: C, 88.35; H, 9.05%.

Compound 11: 2,7-di(4-hydroxyphenyl)-3,6,-10,11-tetra(4-*n*-nonylphenyl)triphenylene

250 mg (88%) of the title compound was isolated as a colourless amorphous solid according to the procedure described for compound **8**. mp 79.5 – 81.5°C **^{1}H NMR** (400 MHz, $CDCl_3$, δ): 8.68 (s, 2H), 8.67 (s, 2H), 8.65 (s, 2H), 7.27 – 7.19 (m, 12H), 7.13 – 7.09 (m, 8H), 6.76 (d, *J* = 8.52 Hz, 4H), 4.69 (s, br, 2H), 2.62 (t, *J* = 7.56 Hz, 8H), 1.64 – 1.59 (m, 8H), 1.38 – 1.20 (m, 48H), 0.91 (t, *J* = 6.48 Hz, 12H); **^{13}C NMR** (100 MHz, $CDCl_3$, δ): 154.4, 141.5, 141.4, 140.0, 139.9, 139.4, 138.9, 134.3, 131.4, 129.9, 128.9, 128.8, 128.76, 128.1, 128.0, 125.5, 125.4, 125.3, 114.9, 35.7, 31.9, 31.4, 29.62, 29.59, 29.56, 29.4, 22.7, 14.13. HRMS (FAB+); *m/z* $[M+H]^+$ calcd for $C_{90}H_{109}O_2$ 1221.8422, found 1222.8540. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}) 3332 (b), 3023, 2922,

2855, 1610, 1512, 1482; Anal. Calcd for $C_{90}H_{108}O_2$: C, 88.47; H, 8.94; Found: C, 88.05; H, 8.85.

Compound 12: Poly-2-(4-dodecyloxyphenyl)-3,6,10,11-tetra(4-*n*-nonylphenyl)-7-oxyphenyl)triphenylene

To a flame dried flask under an argon atmosphere was charged 2,7-di(4-hydroxyphenyl)-3,6,-10,11-tetra(4-*n*-nonylphenyl)triphenylene (0.61 g, 0.50 mmol), 1,12-dibromododecane (0.16 g, 0.50 mmol), caesium carbonate (0.31 g, 0.95 mol) and 1-methl-2-pyrrolidinone (1.07 ml) was heated to 110°C for 24 h. The reaction mixture was allowed to cool to room temperature and water (~10 mL) was added. The suspended solids were extracted with DCM (3 × 150 mL), the combined organics were washed successively with water (2 × 100 mL), dried ($MgSO_4$) and concentrated *in vacuo* to afford the crude polymer (0.74 g). Purification was effected by dissolving the crude in chloroform (2 mL), precipitating with ethanol (6-8 mL) allowing to stand overnight prior to centrifugation (6000 rpm, 20 s). The liquor was decanted and the solids re-dissolved, precipitated and centrifuged a further 4 times. After the final cycle, the solids were dried *in vacuo* to afford the title compound as colourless glassy solid (0.69 g, 96%). Mw = 12,200, Mn = 6700, Mw/Mn = 1.90. IR (ATR) $\bar{\upsilon}_{max}$ (cm^{-1}) 3024, 2926, 2854, 1609, 1576, 1512, 1483. Anal. Found: C, 86.98; H, 9.38%.

4. HATn Mesogens

These were prepared as previously described and showed mp and DSC data in agreement with values previously reported.

5. Preparation of Mixtures between the polymer 12 and the various HATn components

The components (0.03-0.05 g weighed to ±0.001 g) were dissolved in DCM or $CHCl_3$. When required, gentle warming and ultrasonication were used to aid dissolution. The solvent was removed using a rotary evaporator, and the thin film obtained was dried under high vacuum for several days. The dry powdered product was stored under vacuum.

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