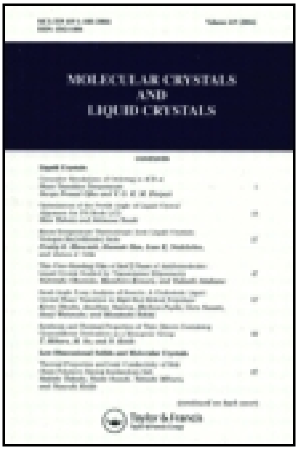

Molecular Crystals and Liquid Crystals

New Functionalised Derivatives of Hexaalkoxytriphenylene

Richard Bushby [a] , Quanying Liu [a] , Owen Lozman [a] , Zhibao Lu [a] & Sholto Mclaren [a]

[a] SOMS Centre, University of Leeds, Leeds, United Kingdom

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NEW FUNCTIONALISED DERIVATIVES OF HEXAALKOXYTRIPHENYLENE

*Richard J. Bushby**, *Quanying Liu, Owen R. Lozman, Zhibao Lu,*
and Sholto R. McLaren
SOMS Centre, University of Leeds, Leeds LS2 9JT,
United Kingdom

We report our latest results on the development of functional triphenylene derivatives. Functionality can be introduced directly into the nucleus by, for example, nitration. Analysis of our recently determined single crystal x-ray structure of 1-nitro-2,3,6,7,10,11-hexaethoxytriphenylene (HAT2-NO$_2$) suggests that the introduced dipole contributes significantly to the stability of the columnar structure. Synthesis of selectively hydroxylated alkoxytriphenylenes allows the functionalisation of one or more side-chains and we show examples of this in which the functional side-chain is: ethyleneoxy or ester or the side chain carries moieties such as: TTF, anthracene, ferrocene, fullerene or crown-ether. The final section details new findings on crown-ether terminated hexaalkoxytriphenylene derivatives, which form lyotropic lamellar phases.

Keywords: discotic liquid crystals; functional materials; substituted triphenylenes; synthesis

INTRODUCTION

Hexaalkoxy derivatives of triphenylene constitute the most important group of discotic liquid crystals [1]. The triphenylene-based discotics have relatively low toxicity and have alignment and charge conduction properties that make them ideal candidates for a range of applications [2]. The synthetic routes required to prepare these triphenylene derivatives are now well established and include routes which enable the synthesis of polymers and functional molecules [3]. The two main ways of achieving this are by electrophilic substitution of the aromatic core or via replacement of one of the side-chains for a functional moiety.

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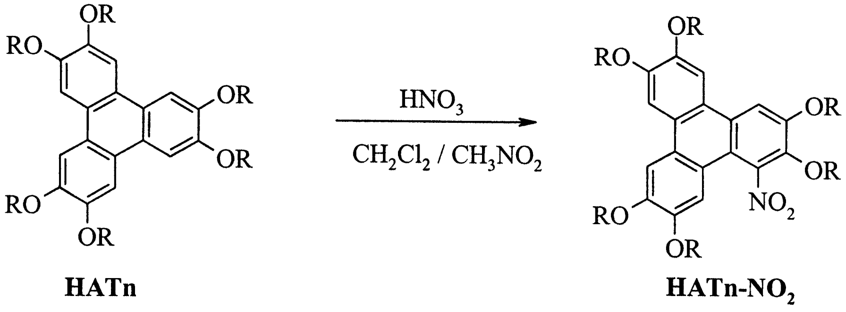
*Corresponding author. E-mail: richardb@chem.leeds.ac.uk



SCHEME 1 Synthesis of HATn-NO_2 from HATn ($R = C_nH_{2n+1}$).

RESULTS AND DISCUSSION

Electrophilic Aromatic Substitution

Electrophilic aromatic substitution has proved a valuable way of modulating the properties of hexasubstituted triphenylene ethers [4]. At the most basic level a strong lateral dipole can be introduced by nitration at the α-position (Scheme 1). This introduces a helical twist into the nucleus and

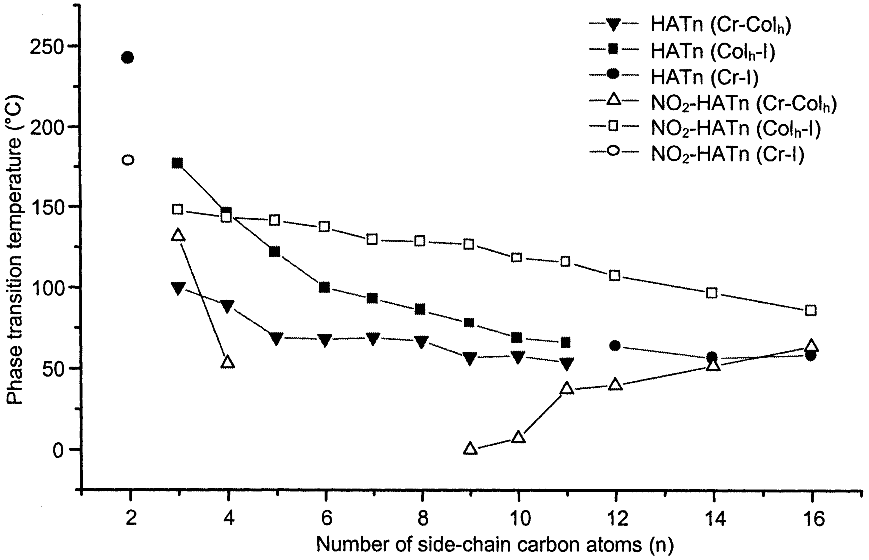


FIGURE 1 The phase transition temperatures of triphenylenes (HATn) and 1-nitrotriphenylenes (HATn-NO_2) as a function of the chain-length (n).

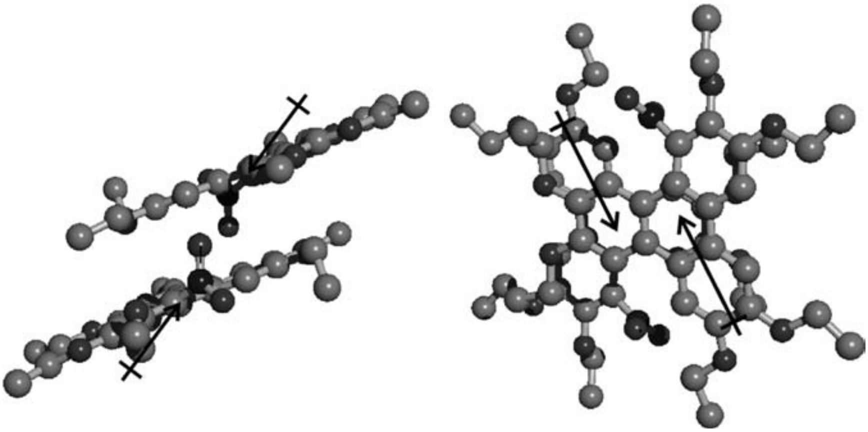


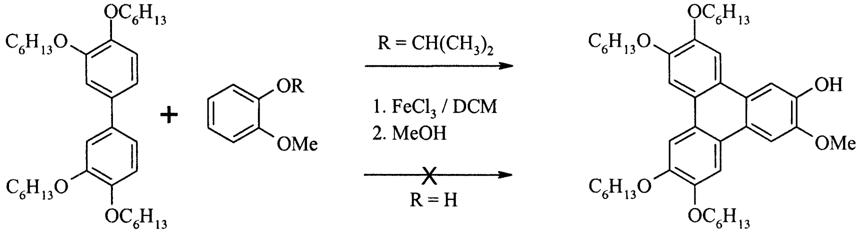
FIGURE 2 An enantiomeric pair or super-disk of HAT2-NO_2 molecules viewed along the crystallographic b (left) and c (right) axes. The dipole moment vectors calculated using DFT [17] (5.96 Debye) are shown by the arrows. This corresponds to an attractive dipole-dipole interaction of $\sim 5\,\mathrm{kJ\,mol^{-1}}$ (in a medium with $\varepsilon_0 \sim 4$).

results in liquid crystals with enhanced mesophase ranges (Fig. 1). The enhanced mesophase range is almost certainly due to strong antiferroelectric dipole-dipole interactions which stabilise the columnar stack. The single crystal X-ray structure of HAT2-NO_2 shows dipole pairing similar to that in cyanobiphenyls and responsible for the re-entrant phases (Fig. 2) [5].

Replacement of a Side-chain

An alternative, more flexible route to functionalised triphenylene-based discotic liquid crystals is to functionally transform one of the alkoxy side chains via the key intermediate mono-hydroxy pentaalkoxytriphenylene **22**. Although there are several routes to this molecule reported in the literature they suffer from poor yields and/or protracted purification procedures [6,7]. We have recently published an improved strategy for the production of selectively hydroxylated alkoxytriphenylenes involving a variant of the phenyl/biphenyl coupling in which an isopropyl moiety is used as a labile blocking or masking group [8]. In the example shown in Scheme 2 the monohydroxy derivative is obtained in 70% yield.

It is important to note that the same product cannot be obtained using a mixture of 2-methoxyphenol and the biphenyl and it is assumed that the isopropyl group is removed in the workup stage of the reaction. With a readily available supply of high purity mono-hydroxy pentaalkoxytriphenylene it is then relatively simple to introduce side chains such as ethyle-



SCHEME 2 The synthesis of mono-hydroxy pentaalkoxytriphenylene **22**.

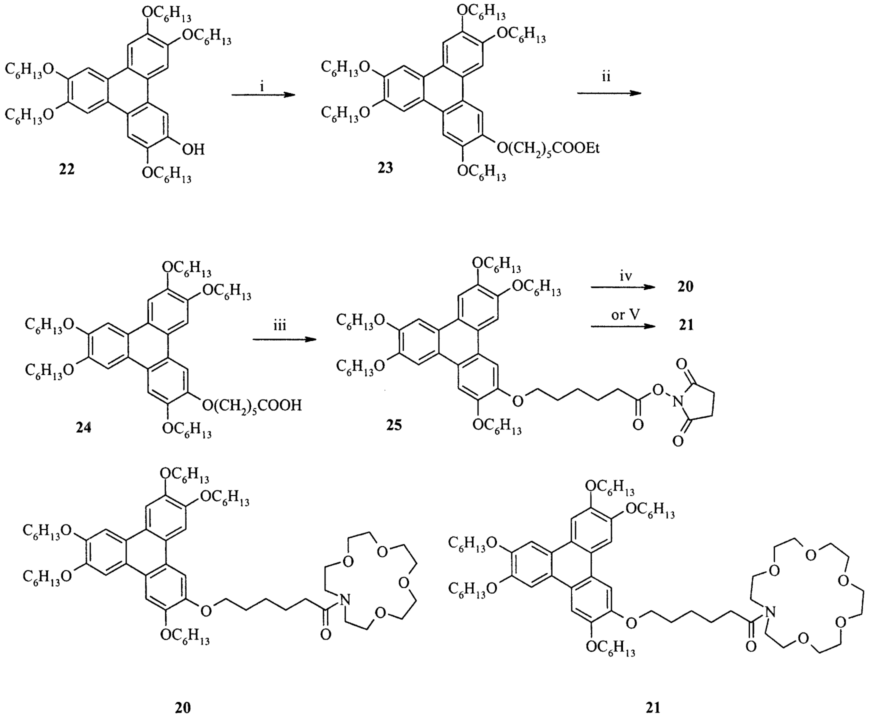
neoxy (**1-3**) [9] or ester-linked (**4-9**) [7]; and side chains bearing terminal groups such as anthraquinone (**10-13**), [10] TTF (**14**), [11] ferrocene (**15-18**, where **10-18** electro-active), [12] fullerene (**19**, potential photoconductor), [13] and crown ethers (**20-21**, potentially responsive to metal ions). Fullerenes [14] and crown ethers [15] covalently linked to calamitic mesogens have been shown to exhibit a rich mesomorphism. In this paper we describe in detail our new results for the crown ether terminated hexahexyloxytriphenylene.

Crown-ether Functionalised Hexaalkoxytriphenylene (20 and 21)

The HAT6-1-aza-15-crown-5 (**20**) and HAT6-1-aza-18-crown-6 (**21**) derivatives were synthesised as shown in Scheme 3. The key step was the preparation of the activated N-hydroxysuccinimidyl ester (**25**).

Differential scanning calorimetry, optical polarising microscopy and X-ray diffraction experiments were performed on the compounds (**20**) and (**21**), their mixtures with excess water ($(\mathbf{20})_{H_2O}$ and $(\mathbf{21})_{H_2O}$) and with excess 1 M aqueous solutions of LiCl, NaCl, KCl and NH_4Cl. As prepared the anhydrous compounds (**20**) and (**21**) exhibit no mesophase. Upon addition of water or one of the aforementioned salt solutions a new material is formed which is mesogenic between ~8 and ~40°C (Table 1). Polarising optical microscopy reveals a grainy, birefringent texture with little long range order and simple shear experiments confirm that the phase has a high viscosity. Thermal analysis shows no difference between the mixtures containing different cations. This suggests that water alone promotes the formation of a mesophase and that the metal ions have little effect. Water-drop penetration experiments reveal the presence of no other phases.

In the mesophase, the low angle x-ray diffraction patterns of $(\mathbf{20})_{H_2O}$ and $(\mathbf{21})_{H_2O}$ show broad, diffuse reflections (Tables 2 and 3). The diffraction patterns of $(\mathbf{20})_{H_2O}$ and $(\mathbf{21})_{H_2O}$ in the mesophase comprise comparable



SCHEME 3 Synthesis of the crown-5 (**20**) and crown-6 (**21**) functionalised triphenylene ethers. i, $Br(CH_2)_5COOEt$, K_2CO_3, EtOH, reflux. ii, NaOH, H_2O, EtOH, reflux, iii, Et_3N, N,N′-disuccinimidyl carbonate, DCM. iv, Et_3N, 1-aza-18-crown-6, DCM, v, Et_3N, 1-aza-15-crown-5, DCM.

maxima, although the peaks are much broader for the crown-5 containing $(\mathbf{20})_{H_2O}$. Both sets of data are consistent with diffraction from a columnar structure with intercolumnar and intracolumnar separations of ~18.5 and 3.7 Å respectively. In both cases there are reflections from alkyl chain

TABLE 1 Phase Behaviour of the Crown-ether Derivatives and Their Mixtures with Excess Water as Determined by DSC and Optical Polarising Microscopy

Material	2nd heat °C (J/g)	1st cool °C (J/g)
(**20**)	Cr 20.4 (17.9) I	I − 8.6 (−17.7) Cr
(**21**)	Cr 22.2 (24.0) I	I − 6.8 (−19.9) Cr
$(\mathbf{20})_{H_2O}$	Cr 8.4 (138.7) M 39.7 (11.2) I	I 19.8 (−5.0) M − 17.7 (−76.9) Cr
$(\mathbf{21})_{H_2O}$	Cr 8.7 (140.3) M 44.3 (3.0) I	I 28.3 (−5.3) M − 15.0 (−124.0) Cr

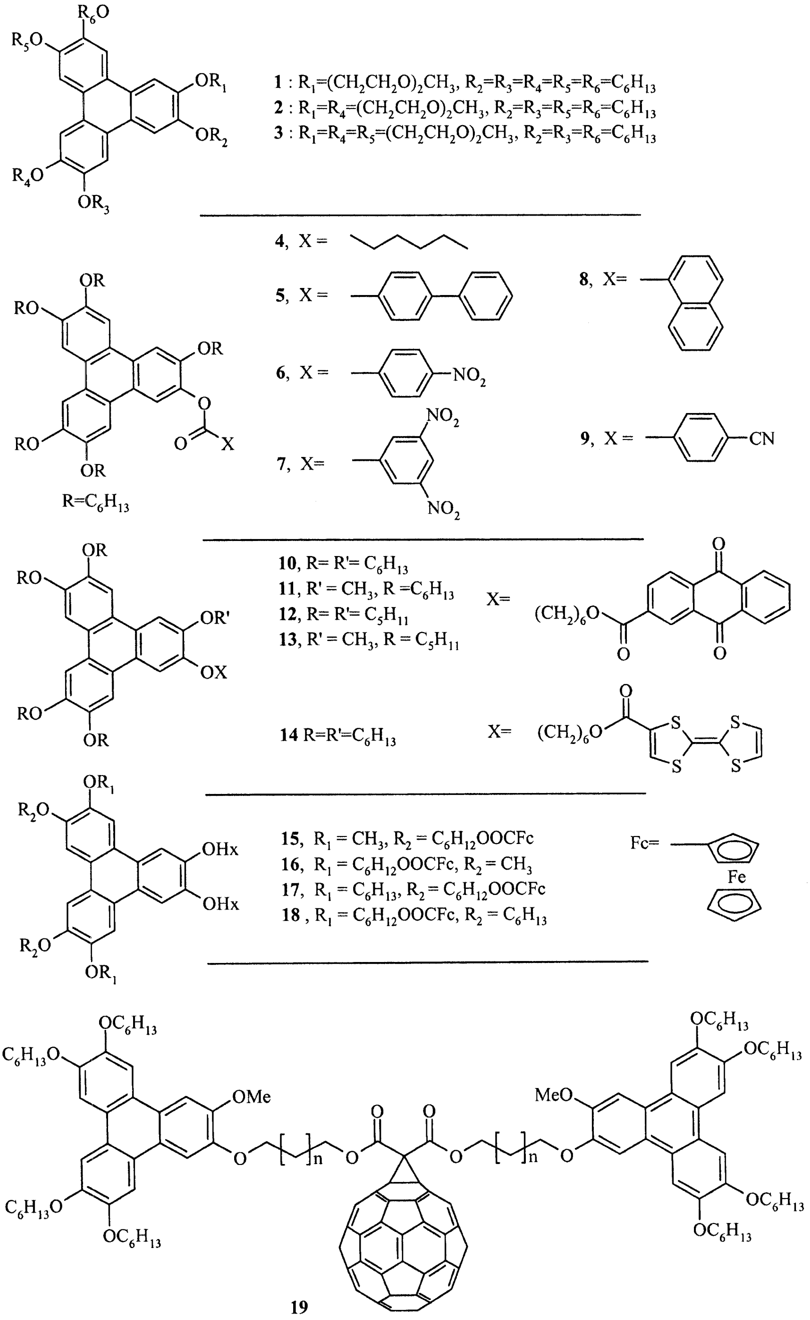


FIGURE 3 Structures of some recently synthesised functional triphenylene derivatives.

TABLE 2 Assignment of the X-ray Powder Diffraction Data for a Sample of HAT6-Crown-5 (**20**) with Excess Water at 35°C (d-spacing Measured in Å)

Miller index	d_{meas} (±0.5 Å)	d_{calc} for orthohombic $a = 28.5$, $b = 18.4$, $c = 3.7$
100	27–30*	28.5
010	18.4	18.4
020	9.3	9.2
040	4.5	4.6
Chain-chain	4.0	~4
001	3.7	3.7

*Very broad, diffuse reflection.

(and water) interactions at ~4.0 Å. In $(\mathbf{20})_{H_2O}$ there is evidence of a weak and very broad reflection at ~27–30 Å possibly due to reflection from lamellae of solvated crown ether (Fig. 3). This lamellar arrangement is strongly visible in $(\mathbf{21})_{H_2O}$ where higher order reflections are consistent with an orthorhombic lattice $a = 27.5$, $b = 18.0$, $c = 3.7$ Å.

An alternative way to view this structure is to consider the molecules (**20**) and (**21**) as conventional hydrophilic head, hydrophobic tail, amphiphiles with additional columnar ordering in the hydrophobic regions. The prominence of higher order reflections from the intercolumnar repeat show that in both cases there is strong coupling between adjacent columns. In unsolvated (**20**) and (**21**) the volume fractions of crown ether are estimated to be 0.16 and 0.19 respectively and no mesophase is observed. In the solvated materials the volume fraction of the crown ether and its associated water would rise to ~0.25 and ~0.30 for $(\mathbf{20})_{H_2O}$ and $(\mathbf{21})_{H_2O}$ with 8 and 10 water molecules respectively. It seems likely that upon increasing

TABLE 3 Assignment of the X-ray Powder Diffraction Data for a Sample of HAT6-crown-6 (**21**) with Excess Water at 40°C (d-spacing measured in Å)

Miller index	d_{meas} (±0.5 Å)	d_{calc} for orthorhombic $a = 27.5$, $b = 18.0$, $c = 3.7$
100	27.5	27.5
010	18.4	18.0
110	14.7	15.1
200	13.8	13.8
020	9.0	9.0
040	4.5	4.5
Chain-chain	4.0	~ 4
001	3.7	3.7

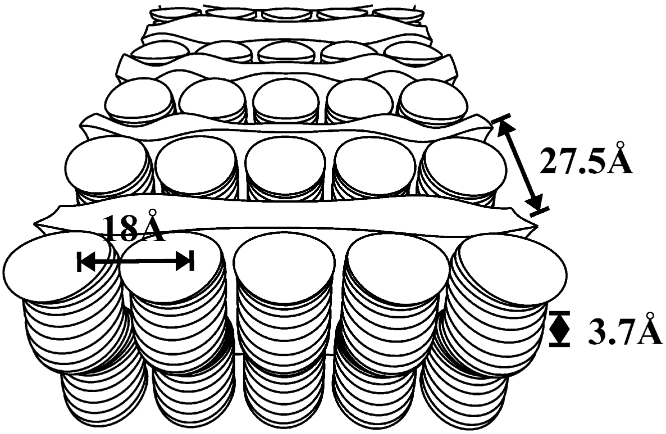


FIGURE 4 Representation of the columnar lamellar structure formed by the HAT6-crown-n derivatives (**20**) and (**21**) when mixed with water.

the volume fraction of crown-ether (by terminating two or more chains with crown-ethers) one would reach a critical value of surface curvature to generate a range of lyotropic phases. In this case one would expect the addition of ions to have a marked effect on the structure and bulk properties of the mesophase [16].

EXPERIMENTAL

General Procedures and Instrumentation

DSC measurements were performed on Perkin-Elmer DSC-7 system (3–5 mg in sealed Al pans under a nitrogen atmosphere, block temperature −40°C, cooling and heating rate 10°C/min). X-ray diffraction patterns were collected on film using a pinhole camera consisting of a Phillips generator and tubes, nickel-filtered Cu K_α radiation of $\lambda = 1.54$ Å, and a Lindemann sample tube (1.5 mm inner diameter) to plate distance of 135.5 mm. Nuclear magnetic resonance spectra were recorded on a Bruker DPX300 spectrometer. Chemical shifts are expressed in parts per million (ppm) downfield of tetramethylsilane for ^{1}H resonance's. Mass spectra were recorded on a VG Autospec mass spectrometer. Microanalyses were carried out at Leeds University Microanalytical Laboratory. All C, H, and N analytical figures are percentage values. Thin layer chromatography was carried out using pre-coated plastic backed silica plates which were visualised under ultraviolet. Flash chromatography signifies column chromatography on Merck silica gel (230–400). Petroleum ether refers to the petroleum fraction with boiling range 40–60°C.

2-(6′-Carboxypentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (24)

2-Hydroxy-3,6,7,10,11-pentahexyloxytriphenylene (**22**) [9] (1.39 g, 1.85 mmol), ethyl-6-bromohexanoate (0.53 g, 2.30 mmol) and potassium carbonate (0.59 g, 4.28 mmol) were refluxed in ethanol (50 ml) for 2 days. The inorganic salts were removed by filtration and washed with DCM. Solvent was removed *in vacuo* and the product (**23**) purified via column chromatography on silica gel using 2:1 petroleum ether: DCM as eluant. Intermediate (**23**) was refluxed overnight in ethanol (20 ml) and water (5 ml), with one pellet of sodium hydroxide. After cooling the mixture was cautiously poured into 1 M HCl (50 ml), extracted with DCM, and the solvents removed *in vacuo*. The product (**24**) (0.98 g, 61%) was purified by column chromatography on silica gel using 1:1 DCM:ethyl acetate as eluant. The title compound (**24**) was obtained as white powder. Subsequent analytical data were in accordance with the literature values [3].

N-hydroxysuccinimidyl ester of 2-(6′-Carboxypentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (25)

2-(6′-Carboxypentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (**24**) (0.50 g, 0.58 mmol), *N,N′*-disuccinimidyl carbonate (0.22 g, 0.87 mmol) and triethylamine (0.23 g, 2.32 mmol) were stirred in DCM (50 ml) overnight. The solvent was removed *in vacuo* and the reaction mixture filtered through silica using DCM as eluant to give the crude product (**25**) which was used in the next step of reaction without further purification. δ_H(300 MHz, $CDCl_3$) 7.83 (6 H, m, Ar*H*), 4.23 (12 H, t, J 6.6, OCH_2), 2.83 (4 H, s, CH_2 on succinimide), 2.69 (2 H, t, J 7.4, CH_2CO), 1.96 – 1.89 (14 H, m, CH_2CH_2O, CH_2CH_2CO), 1.79 – .35 (32 H, m, CH_2), 0.93 (15 H, t, J 6.8, CH_3).

HAT6-1-aza-15-crown-5 derivative (20)

N-hydroxysuccinimidyl ester of 2-(6′-Carboxypentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (**25**, 0.20 g, 0.21 mmol), 1-aza-15-crown-5 (0.11 g, 0.52 mmol) and triethyl amine (0.11 g, 1.05 mmol) were stirred in DCM (50 ml) for 8 hours. The solvent was removed *in vacuo* and the product (**20**) purified by column chromatography on silica gel, eluting with ethyl acetate to yield 0.20 g, 0.19 mmol, 92%. $C_{64}H_{101}NO_{11}$ requires: C, 72.5; H, 9.60; N, 1.32. Found: C, 72.65; H, 9.40, N, 1.50. δ_H(300 MHz, $CDCl_3$) 7.83 (6 H, m, Ar*H*), 4.23 (12 H, t, J 6.6, OCH_2), 3.80 (2 H, t, J 7.0, CH_2N), 3.66 – 3.53 (18 H, m, CH_2O, CH_2N of crown ether), 2.42 (2H, t, J 6.7, CH_2CON), 1.96 – 1.89 (12 H, m, CH_2CH_2O), 1.79 – 1.72 (2H, m, CH_2CH_2CON), 1.65 – 1.55 (10 H, m, CH_2), 1.48 – 1.35 (22 H, m, CH_2), 0.93 (15 H, t, J 6.8, CH_3). MS (ESI) 1083 (100%, $[M+Na]^+$).

HAT6-1-aza-18-crown-6 derivative (21)

N-hydroxysuccinimidyl ester of 2-(6′-Carboxypentyloxy)-3,6,7,10,11-pentahexyloxytriphenylene (**25**, 0.25 g, 0.26 mmol), 1-aza-18-crown-6 (0.10 g, 0.39 mmol) and triethyl amine (0.13 g, 1.30 mmol) were stirred in DCM (50 ml) for 8 hours. The solvent was removed *in vacuo* and the product (**21**) purified by column chromatography on silica gel, eluting with ethyl acetate to yield 0.26 g, 0.23 mmol, 90%. $C_{66}H_{105}NO_{12}$ requires: C, 71.77; H, 9.58; N, 1.27. Found: C, 71.5; H, 9.85, N, 1.20δ_H(300 MHz, $CDCl_3$) 7.83 (6 H, m, Ar*H*), 4.23 (12 H, t, J 6.6, OCH_2), 3.69 – 3.59 (24 H, m, CH_2O, CH_2N of crown ether), 2.43 (2H, t, J 7.2, CH_2CON), 2.01 – 1.92 (12 H, m, CH_2CH_2O), 1.84 – 1.73 (2H, m, CH_2CH_2CON), 1.68 – 1.52 (10 H, m, CH_2), 1.48 – 1.35 (22 H, m, CH_2), 0.94 (15 H, t, J 6.9, CH_3). MS (ESI) 1127 (100%, $[M+Na]^+$).

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