Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Triphenylene/Carbazole Mesogens and Their Electrochemistry

M. Manickam [a], Graeme Cooke [b], Sandeep Kumar [c], Peter R. Ashton [a], Jon A. Preece [a] & Neil Spencer [a]

[a] School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK

[b] Centre for Biomimetic Design and Synthesis, Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS

[c] Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore, 560 013, India

Version of record first published: 18 Oct 2010

To cite this article: M. Manickam, Graeme Cooke, Sandeep Kumar, Peter R. Ashton, Jon A. Preece & Neil Spencer (2003): Triphenylene/Carbazole Mesogens and Their Electrochemistry, Molecular Crystals and Liquid Crystals, 397:1, 99-116

To link to this article: http://dx.doi.org/10.1080/714965597

Mol. Cryst. Liq. Cryst., Vol. 397, pp. 99/[399]–116/[416], 2003

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390214059

Taylor & Francis
Taylor & Francis Group

TRIPHENYLENE/CARBAZOLE MESOGENS AND THEIR ELECTROCHEMISTRY

M. Manickam
School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

Graeme Cooke
Centre for Biomimetic Design and Synthesis, Department of Chemistry, Heriot-Watt University, Riccarton, Edinburgh, EH14 4AS

Sandeep Kumar
Centre for Liquid Crystal Research, P.O. Box 1329, Jalahalli, Bangalore – 560 013, India

Peter R. Ashton, Jon A. Preece, and Neil Spencer*
School of Chemical Sciences, University of Birmingham, Edgbaston, Birmingham B15 2TT, UK

The synthesis of 10 discotic mesogens is described in which the well-known hexaalkyloxytriphenylene liquid crystalline core has been covalently linked to incorporate one and three carbazole moieties. These modifications have been achieved by the esterification of mono and tris hydroxy triphenylene derivatives with carboxylic acids incorporating 3,6-bisalkylated or 3,6-bisacylated carbazole moieties. The pure compounds are not liquid crystalline and neither are they when doped with TNF, unlike similar materials that were reported previously, where the carbazole moiety was not 3,6-bisalklylated or 3,6-bisacylated, which when doped with TNF did display mesophases. The solution state cyclic voltammetry of selected materials is reported.

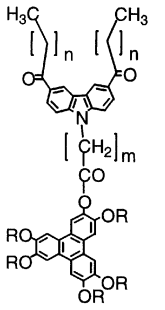
Keywords: carbazole; photorefractive; anisotropic ordering; discotic liquid crysals; electrochemistry

This research has been supported by the (i) Leverhulme Trust (MM), (ii) Perkin-Elmer/HEFCE in the UK through the Joint Research Equipment Initiative (JREI). S. Kumar would like to thank the Royal Society of Chemistry for the award of the Journals Grant for International Authors.

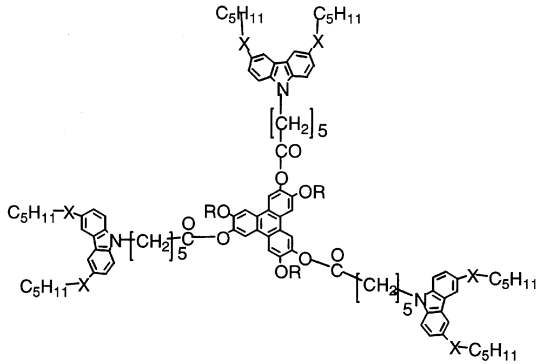
Corresponding author. E-mail: j.a.preece@bham.ac.uk

INTRODUCTION

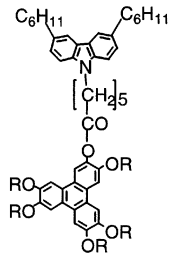
Due to their extensive biological activity carbazole derivatives and their chemistry have been studied at length [1]. However, it is only recently that they have been studied in terms of their material properties [1,2] and in particular their photorefractive properties [3]. The interest in photorefractive materials [4] lies in their numerous potential technological applications [5], such as high density optical data storage, optical image processing, phase conjugated mirrors, dynamic holography, optical computing, parallel optical logic, and pattern recognition. Thus, recent studies on carbazole materials have been concerned with electroluminescence [6], nonlinear optics [7], and photoconductivity [8]. Amorphous organic photorefractive materials [9] have many advantages over crystalline inorganic [3] and latterly crystalline organic [10] photorefactive materials on which the early research was carried out. These advantages include large optical nonlinearities, low dielectric constants, low cost, structural flexibilty, and ease of fabrication. However, the major drawback of the amorphous organic photorefractive materials is that a low T_g is required in order that the material can be aligned by a dc electric field to induce a degree of anisotropic ordering [11]. The chemical modification of the carbazole moiety to induce liquid crystallinity is attractive in order to combine the advantages of the amorphous materials with anisotropic ordering, and subsequent ease of noncentrosymmetric alignment via an applied electric field. However, to date there are only a few examples in which the carbazole moiety has been incorporated into thermotropic low molecular weight and polymeric liquid [12] crystalline materials and into lyotropic liquid crystals [13]. Furthermore, as far as we are aware, there are no examples of low molecular thermotropic hexagonal columnar discotic liquid crystals which incorporate the carbazole. Thus, one of the approaches that we are adopting [14] to induce hexagonal columnar discotic mesophases in carbazole derivatives is the covalent modification of the carbazole moiety with the well-known discotic triphenylene derivatives [15]. Previously, we reported [16] (i) the synthesis of several carbazole triphenylene hybrid structures in which one, two, three and six carbazole units were covalently linked to the periphery of the triphenylene core and (ii) the induced mesophase behaviour of some of these carbazole derivatives when "complexed" with trinitrofluorenone (TNF) [17]. In this present paper we report the synthesis of some similar triphenylene/carbazole mesogens (**1-10**) that have been chemically modified on the 3,6-positions on the carbazole moiety, and their solution electrochemistry. The chemical structures of the carbazole derivatives are shown in Figure 1.



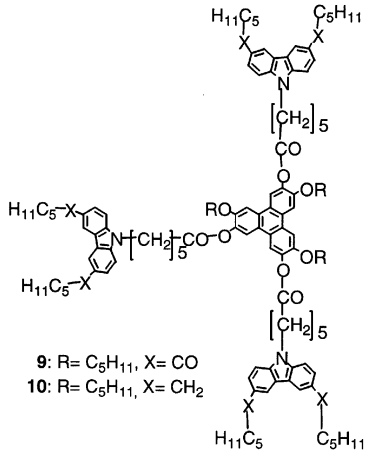
1: R = C_5H_{11}, n = 4, m = 5
2: R = C_5H_{11}, n = 4, m = 10
3: R = C_5H_{11}, n = 14, m = 4
4: R = C_6H_{13}, n = 4, m = 5
5: R = C_7H_{15}, n = 4, m = 5



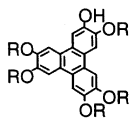
7: R= C_5H_{11}, X= CO
8: R= C_5H_{11}, X= CH_2



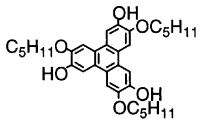
6: R=C_4H_9



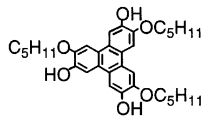
9: R= C_5H_{11}, X= CO
10: R= C_5H_{11}, X= CH_2



11: R= C_4H_9
12: R= C_5H_{11}
13: R= C_6H_{13}
14: R= C_7H_{15}



15



16

FIGURE 1 Tripenylene/Carbazole molecular strctures **1-10** and hydroxytripenylene intermediates **11-16**.

RESULTS AND DISCUSSION

Molecular Design

These new triphenylene/carbazole mesogens were designed to enhance the discotic mesophase supporting ability, *via* the introduction of the two 3,6-alkyl chains or two 3,6-acyl chains to the carbazole moiety, relative to the original molecular structures (of which some are shown in Fig. 2) [16], in which mesophases were only supported when they were doped with TNF. Our reasoning for the introduction of the extra chains on the 3,6 positions of the carbazole was that in the original materials (Fig. 2) [16] it was felt the lack of mesophase of the pure materials was a result of the increased π-surface relative to the alkyl component. Thus, the addition of further chains would restore the π-surface area to alkyl chain balance that may support a mesophase.

Synthesis

Compounds **1-6** in which one carbazole moiety is attached to the triphenylene core relies on coupling of carbazole derivatives to the monohydroxytriphenylene derivatives **11-14**, whilst compound **7-10** which incorporate three carbazole moieties are based on the symmetric and asymmetric trishydroxytriphenylenes **15** and **16**, respectively. The synthesis of these hydroxytriphenylene derivatives are reported in the literature

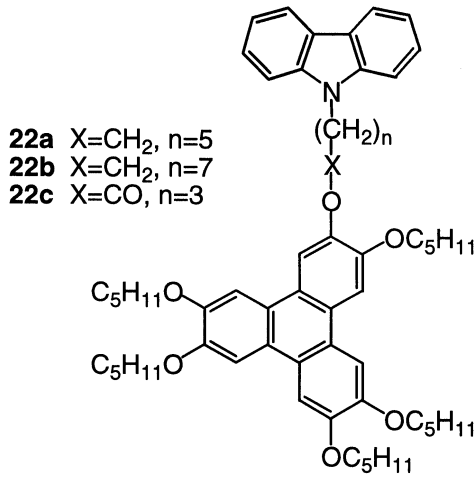
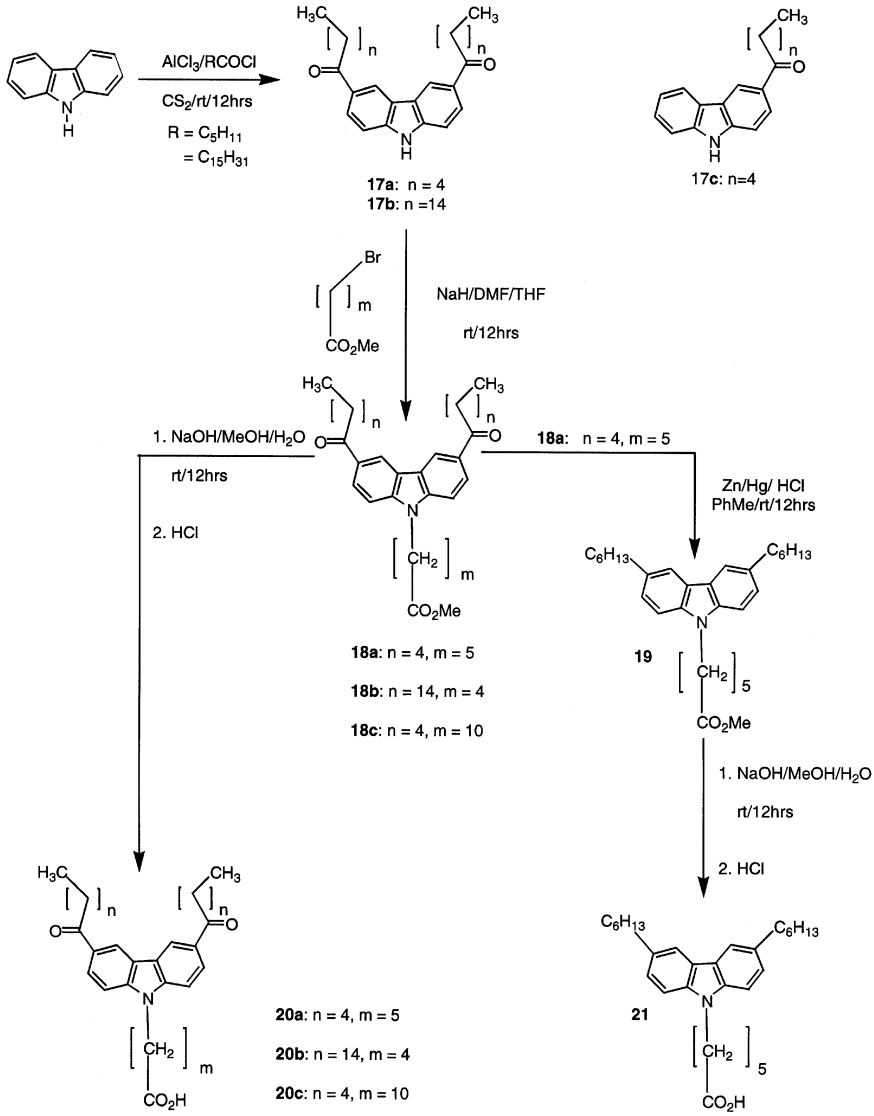


FIGURE 2 Triphenylene/Carbazole molecular structures studied by electrochemistry **22a-c**.

[18]. The Scheme illustrates the synthesis of several acids (**20a-c** and **21**) that are coupled to **11-16** to afford **1-10**. Briefly, carbazole is bisacylated, *via* a Freidel-Crafts conditions [12] with a short chain and long chain acid chloride to afford **17a** and **17b**, respectively. Incidentally, with the short



SCHEME Synthetic routes to the carbazole derivatives **20a-c** and **21**.

chain acid chloride a monoacylated product was isolated (**17c**). These two bisacylated carbazole derivatives were subsequently N-alkylated with two α,ω-bromoesters to afford three **18a-18c**. A zinc/mercury amalgam was then used to reduce the carbonyl functionalities in **18a** to afford the bis-3,6-alkyl derivative **19**. Finally, the four esters **18a-c** and **19** were then hydrolysed to the acids **20a-c** and **21**, respectively. The acids **20a-c** and **21** were then used to form mono- and tris-esters **1-6** and **7-10**, respectively, *via* a DCC coupling with the respective hydroxy triphenylene derivatives **11-16**.

Thermal Properties

The new triphenylene/carbazole derivatives (**1-10**), as single component mixtures, did not show any birefringent liquid phases when observed under the optical polarised microscope. This was not a totally surprising result as none of the compounds that were reported previously [16] exhibited a mesophase as a single component. However, it was expected that doping with trinitrofluorenone (TNF) would induce a mesophase, as it did with the previously reported [16] compounds. Unfortunately, doping experiments of **1-10** with TNF did not produce any mesophases. Thus, our design criteria of the introduction of two alkyl chains or two acyl chains to the carbazole moiety to enhance the discotic mesophase was not correct. It should be pointed out that we have derivatised carbazole [19] at the 3,6 positions to afford banana-shaped liquid crystals. To date, all attempts to induce mesophases in these materials have not suceeded. Thus, a 3,6 substituted carbazole may be inherently non-mesogenic.

Electrochemistry

The chemical modification of discotic triphenylene core with electroactive moieties, such as TTF [20], ferrocene [20], and anthraquinone [21] and studying the resulting electrochemistry has recently been reported [20–21]. These studies have been performed to study the charge transfer complexes that may form with potential applications in rectification and electron transfer. Thus, although not our primary aim in the line of research reported here, we have initiated a similar line of investigation. Indeed such studies, on the materials presented here, will be of interest in view of the fact that the photorefractive effect does rely on the photo-oxidation of the carbazole [3]. Our preliminary study is detailed below.

We have investigated the solution electrochemistry of derivatives [16] **22a-22c** using cyclic voltammetry (CV) (Table 1). All compounds gave similar voltammograms, displaying redox waves consistent with a reversible oxidation sandwiched between two irreversible oxidation waves (Fig. 3).

TABLE 1 CV Data for Compounds **22a-c**

Compound	$E^1_{1/2}$ (Volts)	$E^2_{1/2}$ (Volts)	$E^3_{1/2}$ (Volts)
22a	0.86 (irreversible)	1.14	1.36 (irreversible)
22b	0.85 (irreversible)	1.03	1.29 (irreversible)
22c	0.94 (irreversible)	1.11	1.28 (irreversible)

The reversible oxidation wave is presumably due to the formation of the radical cation state of the triphenylene moiety [22], whereas the irreversible waves are most likely due to the oxidation of the carbazole unit.

CONCLUSIONS

The synthesis of several mesogenic carbazole (**1-10**) derivatives has been described. The pure compounds were found not to be liquid crystalline in nature. Furthermore, it was not possible to induce mesophase formation by doping with TNF. This lack of mesophase formation was in direct contrast to our previous studies in which triphenylene/carbazole hybrid structures when doped with TNF formed mesophases. Once again the delicate balance between molecular structure and bulk structure had defied rational

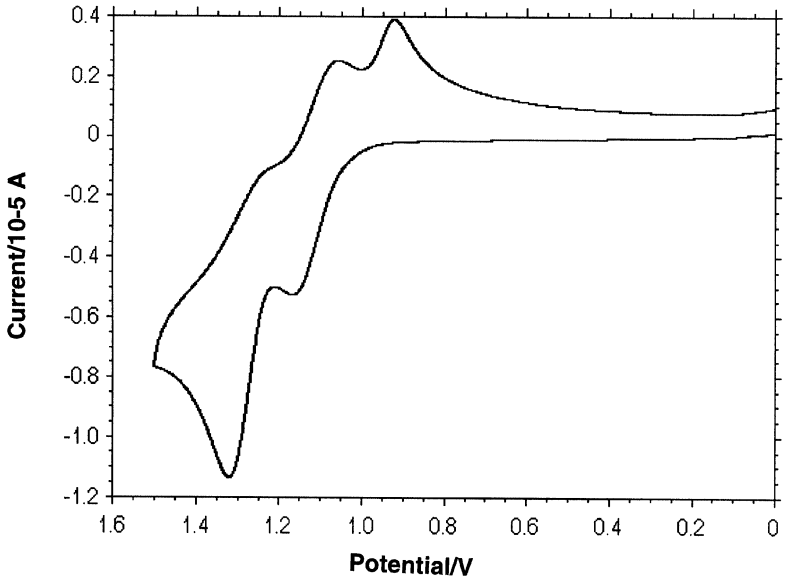


FIGURE 3 Voltammogram for derivative **22c**.

design! The electrochemical evaluation reported in this paper shows that both the triphenylene and carbazole potentials are present. Further, investigations are under way to evaluate the nature of any interactions between the triphenylene and carbazole moieties.

Having now synthesised 23 triphenylene derivatises in which carbazole is linked to the periphery of the triphenylene core *via* a flexible alkyl chain in which only limited success has been gained in creating mesophases, we have concluded that this design approach is no longer worth pursueing. Presently, we are working on the synthesis of two carbazole derivatives illustrated in Figure 4. In these two structures the carbazole moiety is incorporated directly into the discotic core, and as such we feel has a much better chance of supporting a mesophases. However, recently reports [24] of complementary polytopic interactions (CPI) inducing liquid crystallinity in the non-liquid crystalline TTF [20] and ferrocene [21] appended triphenylenes, leads us to believe that the compounds reported here (**1-10**, **22a-c**), may be able to support a mesophase as binary mixtures with large core polynuclear aromatics.

EXPERIMENTAL SECTION

General Methods

Chemicals were purchased from Aldrich and used as received. Yields refer to chromatographically pure products. Thin-layer Chromatography (TLC) was carried out on aluminium sheets coated with silica gel 60 (Merck 5554 mesh). Column chromatography was performed on silica gel 60 (Merck 230–400). Elemental analysis was carried out on a Carlo Erba EA 1110 (CNNS) instrument. Electron impact (EI) mass spectra were recorded at 70 eV on a VG ProSpec mass spectrometer. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG ZapSpec mass spectrometer equipped with a celsium ion source with *m*-nitro-

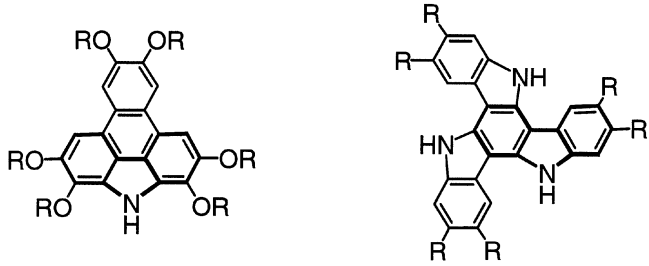


FIGURE 4 Proposed discotic carbazole derivatives.

benzylalcohol containing a trace of sodium acetate. ^{1}H NMR spectra were recorded on a Bruker AC 300 (300 MHz) or a Bruker AMX400 (400 MHz) or a Bruker DRX500 (500 MHz) spectrometer. ^{13}C NMR spectra were recorded on a Bruker AC300 (75.5 MHz) or a Bruker DRX500 (125.8 MHz) spectrometer. The chemical shift values are expressed as δ values and the coupling constant values (J) are in Hertz. The following abbreviations are used for the signal multiplicities or characteristics: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, muliplet; q, quartet; quint; quintet; br, broad. Transition temperatures were measured using a Mettler FP82 HT hot stage and Central processor in conjunction with Leitz DMFRT Polarizing mircroscope as well as differential scanning calorimetry (DSC7 Perkin-Elmer). All CV experiments were performed using a CH120A electrochemical workstation. The electrolyte solution was prepared from recrystallised Bu_4NPF_6 using spectroscopic grade CH_2Cl_2 (0.1 M) and purged with nitrogen prior to use. A three electrode configuration was used with a Pt working electrode, a Ag/AgCl reference electrode and a platinum wire as the counter electrode. Scan rate $= 100\,mVs^{-1}$. $T = 25°C$.

2-hydroxy- 3, 6, 7, 10,11 -pentabutyoxy-triphenylene (**11**), 2-hydroxy 3, 6, 7, 10, 11-pentapentyloxy-triphenylene (**12**), 2-hydroxy 3, 6, 7, 10, 11 -pentahexyloxy-triphenylene (**13**), 2-hydroxy 3, 6, 7, 10, 11- pentaheptyloxy-triphenylene (**14**), symmetrical 2, 6, 10-trihydroxy-3, 7, 11-tris-penty-loxytriphenylene (**15**) and nonsymmetrical 2, 7, 10-trihydroxytripentyloxy-triphenylene (**16**) were synthesized according to literature procedures [17]. The charge transfer complexes of the carbazole triphenylene derivatives with TNF were prepared by dissolving appropriate amount of both compounds separately in dichloromethane, mixing their solutions and evaporating the solvent [ref].

Synthesis of compound 1

To a solution of the carbazole derivative **20a** (0.188 g, 0.38 mmol) in dry CH_2Cl_2 (10 mL) cooled to 0°C under an N_2 atmosphere was added 1,3-dicyclohexylcarbodiimide (0.12 g, 0.59 mmol) and a catalytic amount of 4-dimethylaminopyridine. The mixture was stirred for 30 minutes and 2-hydroxy-3, 6,7,10-pentapentyloxytriphenylene **12** (0.20 g, 0.9 mmol) was added over 10 minutes, followed by further stirring for 24 h under an N_2 atmosphere at room temperature. A white precipitate was filtered and the filtrate was diluted with CH_2Cl_2 (30 mL) and washed with H_2O (3×30 mL), followed by 10% $NaHCO_3$ (10 mL) and saturated NaCl (5 mL). The organic phase was dried over ($MgSO_4$), filtered, and the filtrate evaporated to dryness under reduced pressure. The residue was purified by silica gel column chromatography (eluent: Hexane/CH_2Cl_2, 1:3) to yield **1** (0.130 mg, 40%) as a white solid.

Mp 58°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.71 (s, 1H), 8.71 (s, 1H), 8.10 (d, 1H, $J = 1.5$ Hz), 8.08 (d, 1H, $J = 1.5$ Hz), 7.95 (s, 1H), 7.74 (t, 4H, $J = 7.0$ Hz), 7.66 (s, 1H), 7.35(d, 2 H, $J = 8.7$ Hz), 4. 21 (m, 12H), 3.02 (t, 4H, $J = 7.3$ Hz), 2.62 (t, 2 H, $J = 7.3$ Hz), 1.96 (m, 9H), 1.79 (m, 9 H), 1.57 (m, 8H), 1.47 (m, 8H), 1.39 (m, 14H), 0.94 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.6, 171.4, 149.6, 149.1, 149.0, 148.9, 148.7, 143.5, 139.4, 129.4, 127.7, 126.6, 124.4, 123.1, 123.0, 122.8, 122.8, 121.3, 116.3, 108.6, 107.7, 107.6, 106.4,106.3, 105.7, 69.7, 69.6, 69.3, 69.1, 68.5, 43.0, 38.4, 33.6, 31.6, 29.1, 29.0, 28.9, 28.4, 28.3, 28.0, 26.5, 24.5, 24.3, 22.4, 22.3, 14.0, 13.9. MS (FABMS) m/z 1135 $[M+H]^+$. Found C, 77.07; H, 8.98; N, 1.15%. Calcd for $C_{73}H_{99}NO_9$ C, 77.13, H, 8.88, N, 1.23%.

The same procedure for **1** was followed for the synthesis of **2, 3, 4, 5, 6, 7, 8, 9** and **10**, using the appropriate combination of **11-16** with **20a-c** and **21.**

Compound 2

Mp 63°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.76 (s, 1H), 8.66 (s, 1 H), 8.15 (dd, 2 H, $J = 8.6$, 1.6 Hz), 8.02 (s, 1H), 7.78 (m, 5 H), 7.40 (s, 1H), 7.38 (s, 1 H), 4.22 (m, 12 H), 3.09 (t, 4 H, $J = 7.4$ Hz), 2.65 (t, 2H, $J = 7.4$ Hz), 1.93 (m, 9 H), 1.85 (m, 9H), 1.44 (m, 40H), 0.96 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.8, 171.9, 149.7, 149.4, 149.1, 148.9, 148.7, 143.7, 129.5, 127.8, 126.7, 124.5, 123.3, 123.1, 123.0, 122.9, 122.8, 121.5, 116.6, 108.8, 107.9, 107.1, 106.8, 106.5, 105.9, 69.8, 69.7, 69.4, 69.2, 68.7, 29.3, 29.2, 29.1, 28.9, 28.3, 28.2, 27.2, 24.9, 24.5, 22.5, 14.0, 13.9. MS (FABMS) m/z 1204 $[M+]^+$. Found: C, 77.76; H, 9.13; N, 0.95%. Calcd for $C_{78}H_{109}NO_9$ C, 77.82, H, 9.05, N, 1.16%.

Compound 3

Mp 65°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.78 (s, 1H), 8.79 (s, 1 H), 8.91 (dd, 2 H, $J = 8.6$, 1.6 Hz), 8.00 (s, 1H), 7.81 (m, 4H,), 7.72 (s, 1H), 7.48 (s, 1 H), 7.46 (s, 1H), 4.43 (t, 2H, $J = 7.3$ Hz), 4.21 (m, 10 H), 3.87 (t, 4H, $J = 7.3$ Hz), 2.71 (t, 2H, $J = 7.3$ Hz), 2.11(m, 2H), 1.93 (m, 8H), 1.75 (m, 8 H) 1.55 (m, 10H), 1.48 (m, 10H), 1.32 (m, 48H), 0. 96 (m, 12H), 0.85 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.8, 171.1, 149.8, 149.2, 149.0, 148.8, 143.6, 139.4, 129.7, 128.0, 126.9, 124.6, 123.3, 123.2, 123.1, 123.0, 122.9, 121.6, 116.5, 108.8, 107.9, 107.2, 106.8,106.6, 105.9, 69.8, 69.7, 69.4, 69.2, 68.6, 43.2, 38.6, 33.4, 31.9, 29.6, 29.5, 29.3, 29.1, 28.8, 28.3, 28.0, 24.8, 22.6, 22.5, 22.3, 14.0. MS (FABMS) m/z 1401 $[M+H]^+$ Found: C, 79.08; H, 9. 69; N, 0.87%. Calcd for $C_{92}H_{137}NO_9$ C, 78.92, H, 9.78, N, 1.00%.

Compound 4

Mp 65°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.77 (s, 1H), 8.76 (s, 1 H), 8.15 (d, 1H, $J = 1.5$ Hz), 8.13 (d, 1H, $J = 1.5$ Hz), 7.99 (s, 1H), 7.84 (m, 4H),

7.72 (s, 1H), 7.44 (s, 1 H), 7.46 (s, 1H) 4.38 (t, 2H, $J = 7.3$ Hz), 4.20 (m, 10H), 3.05 (t, 4H, $J = 7.3$Hz) 2.64 (t, 2H, $J = 7.3$ Hz), 1.94 (m, 8H), 1.79 (m, 6H), 1.59 (m, 10H), 1.38 (m, 34H), 0. 94 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.8, 171.5, 149.8, 149.2, 149.3, 149.0, 148.8, 143.6, 139.5, 129.6, 127.9, 126.8, 124.6, 123.3, 123.2, 123.0, 122.9,121.5, 116.5, 108.8, 108.0, 107.3, 106.9, 106.6, 105.9, 69.9, 69.7, 69.5, 69.3, 68.7, 43.3, 38.5, 33.7, 31.6, 29.4, 29.3, 29.2, 28.6, 26.7, 25.8, 25.6, 24.6, 24.4, 22.6,14.0 MS (FABMS) m/z 1205 $[M+H]^+$. Found C, 77.69; H, 9.38; N, 1.12%. Calcd for $C_{78}H_{109}NO_9$ C, 77.76, H, 9.21, N, 1.16%.

Compound 5

Mp 63°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.77 (s, 1H), 8.76 (s, 1H), 8.15 (d, 1 H, $J = 1.5$ Hz), 8.13 (d, 1H, $J = 1.5$ Hz), 7.99 (s, 1H), 7.80 (m, 4H), 7.72 (s, 1 H), 7.44 (s, 1H), 7.42 (s, 1H), 4.38 (t, 2H, $J = 7.0$ Hz), 4.21 (m, 10H), 3.04 (t, 4H, $J = 7.3$ Hz), 2.64 (t, 2 H, $J = 7.3$ Hz), 1.95 (m, 10H), 1.78 (m, 8 H) 1.59 (m, 10H), 1.40 (m, 20H), 1.33 (m, 20H), 0.91 (m, 21H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C). δ 199.7, 171.4, 149.7, 149.2, 149.2, 149.0, 148.8, 143.6, 139.5, 129.6, 127.9, 126.8, 124.6, 123.3, 123.2, 123.0, 122.9, 121.5, 116.5, 108.8, 108.0, 107.2,106.9, 106.6, 105.9, 69.9, 69.7, 69.4, 69.2, 68.7, 43.2, 38.5, 33.7, 31.8, 31.6, 29.4, 29.3, 29.1, 28.6, 26.6, 26.1, 25.9, 24.6, 24.4, 22.5, 14.0, 13.9. MS (FABMS). m/z 1275$[M+H]^+$: Found C, 78.13; H, 9. 44; N, 1.04%. Calcd for $C_{83}H_{119}NO_9$ C, 78.23, H, 9.40, N, 1.09%.

Compound 6

Mp 70°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.01 (s, 1H), 7.86 (s, 5 H), 7.77 (br s, 1 H), 7.26 (m, 5H), 4.30 (t, 2 H, $J = 14.2$ Hz), 4.21 (m, 12H), 2.76 (t, 4 H, $J = 14.2$ Hz), 2.64 (t, 2 H, $J = 14.2$ Hz), 1.92 (m, 14H), 1.60 (m, 14 H), 1.31 (m, 14 H), 1.04 (m, 15H), 0.88 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 171.7, 149.7, 149.4, 149.2,148.9, 148.8, 139.7, 139.1, 133.1, 127.9, 126.1, 124.6, 123.4, 123.2, 123.1, 123.0, 122.8, 119.6, 116.6, 108.1, 107.3, 107.0, 106.7, 105.9, 69.6, 69.4, 69.2, 69.0, 68.4, 42.9, 36.0, 33.9, 32.3, 31.8, 31.4, 31.4, 31.3, 29.0, 28.8, 26.9, 24.8, 22.6, 19.3, 19.2, 14.1, 13.9. MS (FABMS) m/z 1035$[M+H]^+$.

Compound 7

Mp 92°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.73 (d, 6H, $J = 1.3$ Hz), 8.13 (d, 3 H, $J = 1.3$ Hz), 8.11 (d, 3H, $J = 1.3$ Hz), 7.83 (br s, 4H), 7.49 (br s, 4 H), 7.42 (br s, 2H), 7.40 (br s, 2 H), 4.34 (t, 6H, $J = 7.0$ Hz), 4.00 (t, 6 H, $J = 6.5$ Hz), 3.02 (t, 12H, $J = 7.3$ Hz), 2.61(t, 6H, $J = 7.3$ Hz), 1.96 (m, 6H), 1.88 (m, 6 H), 1.75 (m, 12H), 1.58 (m, 6H), 1.36 (m, 42H), 0.89 (m, 27H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.7, 171.3, 149.7, 143.6, 139.4, 129.6, 128.2, 126.8, 122.9, 122.0, 121.5, 117.1, 108.7, 105.6, 43.2, 38.4, 33.8, 31.6, 28.9, 28.6, 28.1, 26.7, 24.7, 24.4, 22.5, 22.4, 14.0, 13.9 MS (FABMS) m/z

1913 $[M]^+$. Found C, 77.00; H, 8.14; N, 2.10%. Calcd for $C_{123}H_{153}N_3O_{15}$ C, 77.20; H, 8.05; N, 2.19%.

Compound 8

^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 7.89 (br s, 6H), 7.87 (s, 3 H), 7.52 (br s, 3H), 7.26 (m, 14H), 4.28 (t, 6H, $J = 7.0$ Hz), 4.07 (t, 6 H, $J = 7.0$ Hz), 2.77 (t, 12H, $J = 7.4$ Hz), 2.62 (t, 6 H, $J = 7.4$ Hz), 1.96 (t, 8 H, $J = 7.4$ Hz), 1.89 (t, 8 H, $J = 7.4$ Hz), 1.80 (t, 8H, $J = 7.0$ Hz), 1.70 (m, 10H), 1.59 (m, 8H), 1.44 (m, 8 H), 1.37(m, 10H), 1.32 (m, 22H), 0.93 (m, 27H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 171.6, 149.5, 139.3, 139.1, 133.2, 128.3, 126.1, 122.8, 122.0, 119.6, 117.3, 108.2, 108.1, 105.8, 36.1, 36.0, 33.9, 32. 3, 31.8, 29.0, 28.8, 28.1, 26.9, 25.0, 22.6, 22.5. MS (FABMS) m/z 1828 $[M+H]^+$.

Compound 9

Mp 78°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.72 (m, 6H), 8.11(m, 6 H), 7.88 (s, 1H), 7. 82 (s, 1H), 7.80 (s, 1H), 7.64 (brs, 1H), 7.63 (s, 1H), 7.52 (s, 1H), 7.38 (m, 6H), 4.30 (m, 6H), 4.09 (t, 4 H, $J = 6.3$ Hz), 4.02 (t, 2H, $J = 6.3$ Hz), 3.02 (m, 12H), 2.62 (m 6 H), 1.92 (m, 6H), 1. 87 (m, 6 H), 1.77 (m, 18H), 1.55 (m, 6H), 1.39 (m, 36H), 0.91(m, 27H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.7, 171.3, 171.2, 149.9, 149.5, 149.4, 146.1, 143.5, 140.4, 140.2, 139.8, 129.4, 128.0, 127.2, 127.0, 126.7, 123.3, 123.1, 122.8, 122.2, 121.4, 116.9, 116.6, 116.4, 109.1, 108.7, 106.1, 106.0, 105.5, 69.0, 68.8, 68.6, 68.6, 68.5, 43.1, 38.4, 34.0, 33.6, 31.6, 29.6, 29.3, 28.9, 28.5, 28.1, 28.0, 26.6, 24.8, 24.5, 24.4, 22.5, 22.4, 13.9. MS (FABMS) m/z 1913 $[M]^+$. Found: C, 77.06; H, 8.13; N, 1.95%. Calcd for $C_{123}H_{153}N_3O_{15}$ C, 77.20, H, 8.05, N, 2.19.

Compound 10

^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.00 (s, 1H), 7.97 (s, 1H), 7.90 (s, 1H), 7.88 (s, 8H), 7. 81 (s, 1H), 7.76 (s, 1H), 7.66 (s, 1H), 7.27 (s, 12H), 4.28 (t, 4H, $J = 7.0$ Hz), 4.23 (t, 2 H, $J = 6.4$ Hz), 4.14 (t, 6H, $J = 6.4$ Hz), 2.77 (t, 12H, $J = 7.4$ Hz), 2.64 (t, 6 H, $J = 7.4$ Hz), 1.88 (m, 10H), 1.70 (m, 20 H), 1.63 (m, 10H), 1.33 (m, 42 H), 0.93 (m, 27H). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 171.7, 150.0, 149.4, 146.5, 145.3, 139.7, 139.6, 139.1, 133.1, 128.7, 127.6, 126.1, 123.5, 123.2, 122.9, 122.8, 122.4, 119.6, 116.9, 116.4, 108.1, 107.5, 105.9, 140.3, 42.9, 36.0, 33.9, 32.3, 31.8, 29.6, 29.0, 28.9, 28.8, 28.3, 28.2, 28.1, 27.0, 24.8, 22.6, 22.4, 14.1, 14.0. MS (FABMS) m/z 1828 $[M+H]^+$.

Synthesis of Compound 17a

A mixture of carbazole (5 g, 29.9 mmol) and $AlCl_3$ (8.7 g, 65.8 mmol) in anhydrous CS_2 (100 ml) was heated under reflux. Heaxonaic acid chloride (8.8 g, 65.8 mmol) was added drop wise over an hour. The reaction mixture was heated until cessation of HCl (tested with litmus paper) evolution (30 h) and the solvent was removed by distillation. The residue was added to

crushed ice and treated with conc. HCl (5 ml) followed by further dilution with water (100 ml). The solid residue was filtered and washed with H_2O and then with a small volume of EtOH. After drying in air, the crude product was recrystallized from EtOH to give **2** (2.5 gm, 23%) as a pure colourless solid.

Mp 195–198°C, ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 11.87 (s, 1H), 8.97 (br d, 2H, $J = 1.6$ Hz), 8.06 (d, 2H, $J = 1.6$ Hz), 8.04 (br d, 2H, $J = 1.6$ Hz), 3.10 (t, 4H, $J = 7.2$Hz), 2.49 (m, 4H), 1.36 (m, 8H), 0.88 (m, 6 H).^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.1, 143.1, 128.9, 126.1, 122.5, 122.1, 111.2, 40.1, 39.9, 39.7, 39.5, 39.2, 39.0, 38.8, 37.6, 31.0, 24.0, 22.0, 13.8. MS (FABMS) m/z 364 $[M + H]^+$. Found: C, 79.39; H, 8.30; N, 3.83%. Calcd for $C_{24}H_{29}NO_2$ C, 79.35, H, 8.06, N, 3.86%.

The same procedure for **17a** was followed for the synthesis of **17b**.

Compound 17b

Mp 180–183°C, ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.79 (s, 2H), 8.15 (dd, 2H, $J = 8.5$, 2.0 Hz), 7.50 (br d, 2H, $J = 8.5$ Hz), 3.12 (t, 4H, $J = 7.3$ Hz), 1.86 (m, 4H), 1.26 (m, 48H), 0.88 (t, 6 H, $J = 7.3$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 143.1, 130.4, 1267.1, 127.0, 123.5, 121.6, 110.8, 110.7, 38.8, 38.6, 38.5, 31.9, 29.9, 29.5, 29.3, 25.0 24.9, 24.7, 22.6, 14.0. MS (FABMS) m/z 644 $[M+H]^+$.

Compound 17c

Mp 260–262°C, ^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25°C) δ 11.60 (s, 1H), 8.20 (m, 2H), 8.07 (s, 1H), 7.79 (d, 1H, $J = 8.2$ Hz), 7.53 (d, 1H, $J = 8.2$ Hz), 7.45 (t, 1H, $J = 7.2$Hz), 7.19 (t, 1H, $J = 7.2$ Hz), 3.09 (t, 2H, $J = 7.2$ Hz), 1.66 (m, 2H, $J = 7.2$ Hz), 1.33 (t, 4H, $J = 3.4$ Hz), 0.88 (t, 3 H, $J = 7.0$ Hz).^{13}C NMR (100 MHz, $(CD_3)_2SO$, 25°C) δ 199.1, 141.1, 139.1, 133.9, 126.9, 125.9, 121.5, 121.0, 120.0, 119.0, 118.3, 111.3, 110.9, 37.9, 30.9, 23.8, 22.0, 13.8. MS (FABMS) m/z 266 $[M+H]^+$. Found: C, 81.13; H, 6.82; N, 4.78%. Calcd for $C_{18}H_{19}NO$ C, 81.50, H, 7.16, N, 5.26%.

Synthesis Of Compound 18a

To a solution of **17a** (1.0 g, 2.7 mmol), in DMF: THF (1: 2, 25 mL) was added sodium hydride (0.098 g, 4.1 mmol, 60% in oil) at room temperature. The mixture was stirred for 15 minutes before addition of bromohexanoicmethylester (1.1 g, 5.5 mmol) and was stirred for 10 h. The reaction was quenched with MeOH (25 mL) and mixture evaporated to dryness. The residue was partitioned between CH_2Cl_2(50 mL) and 3 M HCl aq (50 mL). The organic layer was separated and washed with H_2O (60 mL), dried with anhydrous Na_2SO_4, filtered and the filtrate was evaporated to dryness and the residue was subjected to silica gel column chromatography (eluent: Hexane/CH_2Cl_2, 1:1) to afford **18a** (700 mg, 52%) as a white microcrystalline solid.

Mp 60–63°C, ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.71 (s, 1H), 8.73 (s, 1H), 8.11 (dd, 2H, $J = 8.6$, 1.3 Hz), 7. 36 (s, 1H), 7.35 (s, 1H), 4.26 (t, 2H, $J = 7.1$ Hz), 3.58 (s, 3H), 3.04 (t, 4H, $J = 7.4$ Hz), 2.23 (t, 2 H, $J = 7.3$ Hz), 1.78 (m, 6H), 1.62 (m, 2H), 1.37 (m, 10H), 0.89 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.1, 173.5, 143.5, 129.4, 126.6, 122.7, 122.6, 121.4, 108.7, 51.3, 43.1, 38.4, 33.5, 31.5, 28.4, 26.5, 24.3, 22.4, 13.8. MS (FABMS) m/z 492 $[M+H]^+$. Found: C, 75.82; H, 8.53; N, 2.73%. Calcd for $C_{31}H_{41}NO_4C$, 75.73, H, 8.40, N, 2.84%.

The same procedure for **18a** was followed for the synthesis of **18b** and **18c**.

Compound 18b

Mp 65–67°C,^{1}H NMR (500 MHz, $CDCl_3$, 25°C) δ 8.80 (s, 2H), 8.18 (d, 2H, $J = 8.6$ Hz), 7.45 (d, 2H, $J = 8.6$, Hz), 4.39 (t, 2H, $J = 7.2$ Hz), 3. 65 (s, 3H), 3.12 (t, 4H, $J = 7.2$ Hz), 2.35 (t, 2H, $J = 7.2$Hz), 1.96 (m, 2H), 1.83 (m, 4H), 1.73 (m, 2 H), 1.37 (m, 48H), 0.89 (t, 6H, $J = 6.5$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C): δ; 199.9, 173.3,143.7, 129.7, 126.9, 123.0, 121.6, 108.8, 51.6, 43.2, 38.6, 33.4, 31.9, 29.7, 29.5, 29.3, 29.1, 28.3, 24.8, 22.6, 22.4, 14.0. MS (FABMS) m/z 758 $[M+H]^+$. Found: C, 79.03; H, 10.39; N, 1.67%. Calcd for $C_{50}H_{79}NO_4C$, 79.27; H, 10.43; N, 1.89%.

Compound 18c

Mp 65–67°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.76 (s, 1H), 8.75 (s, 1H), 8.15 (dd, 2H, $J = 8.6$, 1.6 Hz), 7.42 (d, 2H, $J = 8.6$ Hz), 4.29 (t, 2H, $J = 7.3$ Hz), 3.63 (s, 3H), 3.08 (t, 4H, $J = 7.3$ Hz), 2.25 (t, 2H $J = 7.3$ Hz), 1.83 (m, 6 H), 1.56 (t, 2H, $J = 7.0$ Hz), 1.37 (m, 18H), 0.92 (t, 6H, $J = 7.0$Hz).^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 199.83, 173.3, 143.7, 129.5, 126.7, 123.0, 121.5, 108.8, 51.3, 43.5, 38.5, 34.0, 31.6, 29.3, 29.2, 29.0, 29.1, 28.8, 27.1, 24.8, 24.4, 22.4, 14.0. MS (FABMS) m/z 562 $[M+H]^+$. Found: C, 75.64; H, 9.00; N, 2.16%. Calcd for $C_{36}H_{51}NO_4C$, 75. 50: H, 8.89; N, 2.44%.

Compound 20a

A solution of compound **18a** (0.500 g, 1.87 mmol) in MeOH (100 mL) was stirred heated under reflux and a solution of sodium hydroxide (0.112 g, 2.80 mmol) in H_2O (10 mL) was added and heating continued for 6 h. After cooling, the reaction mixture was poured onto crushed ice. The precipitate which formed on acidification with dilute hydrochloric acid was then extracted with Et_2O (3×50 mL). The combined organic layers were washed with H_2O (5 mL) and brine (5 mL), and dried ($MgSO_4$). Filtration and evaporation of the filtrate gave the crude product which was purified by silica gel column chromatography (eluent: n-hexane/EtOAc) to yield the acid **20a** as a white solid (800 mg, 82%).

Mp 99–101°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 11-10 (OH, br envelope), 8.75 (d, 2H, $J = 1.4$ Hz), 8.12 (dd, 2H, $J = 8.6$, 1.4 Hz), 7.40 (s, 1H), 7.38 (s, 1H), 4.30 (t, 2H, $J = 7.4$ Hz), 3.06 (t, 4H, $J = 7.4$ Hz), 2.31(t, 2H, $J = 7.3$ Hz), 1.79 (m, 8H), 1.39 (m, 10H), 0.71 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 178.8, 143.6, 129.5, 126.8, 122.9, 121.5, 108.8, 43.2, 38.4, 33.6, 31.6, 28.5, 26.5, 24.4, 24.2, 22.5, 13.9. MS (FABMS) m/z 478 $[M+H]^+$. Found: C, 75.31; H, 8.23; N, 2.87%. Calcd for $C_{30}H_{39}NO_4C$, 75.49, H, 8.17, N, 2.93%.

The same procedure for **20a** was followed for the synthesis of **20b, 20c** and **21.**

Compound 20b

Mp 104–106°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.77 (s, 1H), 8.77 (s, 1H), 8.14 (dd, 2H, $J = 8.6$, 1.6 Hz), 7.43 (d, 2H,$J = 8.6$ Hz), 4.36 (t, 2H, $J = 7.1$ Hz), 3.08 (t, 4H, $J = 7.2$ Hz), 2.37 (t, 2H, $J = 7.2$ Hz), 1.94 (m, 2H), 1.75 (m, 6H),1.36 (m, 50H), 0.86 (t, 6H, $J = 6.64$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 178.2, 143.6, 129.0, 126.9, 122.9, 121.6, 108.8, 43.1, 38.6, 33.3, 31.9, 29.6, 29.5, 29.3, 28.2, 24.8, 22.6, 22.1, 14.0. MS (FABMS) m/z 744 $[M+H]^+$. Found: C, 79. 27; H, 10.41; N, 1.54%. Calcd for $C_{49}H_{77}NO_4C$, 79.21; H, 10.36; N, 1.88%.

Compound 20c

Mp 82–85°C, ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 8.78 (s, 1H), 8.77 (s, 1H), 8.17(dd, 2H, $J = 8.6$, 1.6 Hz), 7.44 (d, 2H, $J = 8.6$ Hz), 7.42 (s, 1H), 4.32 (t, 2H, $J = 7.2$ Hz), 3.10 (t, 4H, $J = 7.2$ Hz), 2.31(t, 2H, $J = 7.2$ Hz), 1.83 (m, 6H), 1.58 (m, 2H), 1.37 (m, 22H), 0.93 (t, 6H, $J = 7.0$ Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 178.2, 143.7, 129.5, 126. 8, 122.9, 121.6, 108.9, 43.5, 38.5, 33.8, 31.6, 29.3, 29.2, 29.3, 28.9, 28.8, 27.1, 24.6, 24.5, 22.6, 14.0. MS (FABMS) m/z 548 $[M+H]^+$. Found: C, 77.33; H, 8.76; N, 2.45%. Calcd for $C_{35}H_{49}NO_4C$, 77.29, H, 8.75, N, 2.50%.

Compound 19

A mixture of amalgamated Zinc (prepared by a standard procedure) [Ref], from granular zinc (40 g) and 5% aqueous $HgCl_2$(80 ml), **18a** (6.0 g, 12.1 mmol) and conc.HCl (25 ml) was vigorously stirred for 5 min and left to stand overnight. After addition of PhMe (50 ml) the mixture was heated under reflux with stirring for 30 h. After cooling, the liquid phase was decanted and repeatedly extracted with Et_2O. The solid residue was washed with Et_2O and the combined organic extracts were washed with 4% HCl, water, and saturated aqueous $NaHCO_3$ and then dried over Na_2SO_4. The residue obtained from roto-evaporation of the solvent was triturated with ethanol which was then separated by filtration and the solid residue dried under vacuum. The crude material was purified by column chro-

matography on silica gel (CH_2Cl_2/petroleum ether 2:5 as eluent), yielding **19** (1.5 g,37%) as a pure colourless oil ^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 7.87 (s, 2H), 7.27 (brs, 4H), 4.24 (t, 2H, $J = 14.2$ Hz), 3.64 (s, 3H), 2.79 (t, 4 H, $J = 7.4$ Hz), 2.28 (t, 2H, $J = 7.4$ Hz), 1.87 (m, 2H), 1.71 (m, 6H), 1.36 (m, 14H), 0.91 (6H, br m). ^{13}C NMR (100 MHz, $CDCl_3$, 25°C) δ 174.0, 139.1, 133.1, 126.1, 122.7, 119.6, 108.4, 108.1, 51.4, 42.8, 36.0, 33.8, 32.3, 31.8, 29.0, 28.7, 26.8, 24.6, 22.6, 14.1. MS (FABMS) m/z 463 $[M]^+$. Found: C, 80.16; H, 9.89; N, 3.02%. Calcd for $C_{31}H_{45}NO_2C$, 80.36; H, 9.71; N, 3.02%.

Compound 21

^{1}H NMR (400 MHz, $CDCl_3$, 25°C) δ 12.9 (OH, br envelope), 7.89 (s, 2H), 7.27 (s, 4H), 4.25 (t, 2H, $J = 7.3$ Hz), 2.79 (t, 4 H, $J = 7.3$ Hz), 2.33 (t, 2H, $J = 7.3$ Hz), 1.96 (t, 2H, $J = 7.3$ Hz), 1.70 (m, 6H), 1.38 (m, 15H), 0.91 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.6, 139.1, 133.1, 126.4, 126.1, 122.7, 121.3, 119.6, 119.2, 116.9, 108.5, 108.1, 42.8, 36.0, 33.7, 32.3, 31.8, 29.6, 29.0, 28.7, 27.5, 27.2, 26.7, 24.4, 22.6, 14.1. MS (FABMS) m/z 449 $[M]^+$. Found: C, 80.32; H, 9.44; N, 3.28% Calcd for $C_{30}H_{43}NO_2C$, 80.19; H, 9.56; N, 3.12%.

REFERENCES

[1] (a) Link, J. T., Raghavan, S., Gallant, M., Danishefsky, S., Chou, T. C., & Ballas, L. M. (1996). *J. Am. Chem. Soc.*, *118*, 2825.
(b) Yamashita, Y., Fujii, N., Murkata, C., Ashiawa, T., Okabe, M., & Nakano, H. (1992). *Biochemistry*, *31*, 12069.
(c) Chakraborty, D. P. (1997). *Prog. Chem. Org. Nat. Prod.*, Vol. 34, Heiz, W., Grisebach, H., & Kirby, G. W. Springer: Wien, 299.

[2] Zhang, Y., Wada, T., & Sasabe, H. (1998). *J. Mater. Chem.*, *8*, 809.

[3] The space charge field induced photorefractive effect was first observed in inorganic electro-optic $LiNbO_3$ crystals by Ashkin, A., Boyd, G. D., Dziedic, J. M., Smith, R. G., Ballman, A. A., & Nassau, K. (1966). *Appl. Phys. Lett.*, *9*, 72.

[4] The first report of a carbazole containing photorefractive material was by Zhang, Y., Cui, Y., & Prasad, P. N. (1992). *Phys. Rev. B*, *46*, 9900.

[5] Günter, P. & J.-P. Huignardm, Eds. *Photorefractive Materials and Their Applications*. Springer-Verlag: New York, 1988.

[6] Maruyama, S., Tao, X.-t., Hokari, H., Noh, T., Zhang, Y., Wada, T., Sasabe, H., Watanabe, T., & Miyata, S. (1999). *J. Mater. Chem.*, *9*, 893.

[7] Zhang, Y., Wang, L., Wada, T., & Sasabe, H. (1996). *Chem. Commun.*, 559.

[8] Scott, J. C., Pautmeier, L. Th., & Moerner, W. E. (1992). *J. Opt. Soc. Am. B*, *9*, 2059.

[9] The first report of an amorphous organic photorefractive material was by Ducharme, S., Scott, J. C., Twieg, R. J., & Moerner, W. E. (1991). *Phys. Rev. Lett.*, *66*, 1846.

[10] Sutter, K., Hulliger, J., & Günter, P. (1990). *Solid State Chem.*, *74*, 867.

[11] Zhang, Y., Wada, T., Wang, L., & Sasabe, H. (1997). *Chem. Mater.*, *9*, 2798.

[12] The carbazole moiety has been introduced into a low molecular weight calamitic mesogenic structure which diplays a nematic mesophase, see Lux, M. & Strohriegl, P. (1987). *Makromol. Chem.*, *188*, 811. Additionally, a report of a polydiacetylene incorporating pendant carbazole moieties has been shown to organise into a self-organised structure,

with columnar mesophases from room temperature to 250°C, see: Gallot, B., Cravino, A., Moggio, I., Comoretto, D., Cuniberti, C., Dell'erba, C., & Dellepiane, G. (1999). *Liq. Cryst.*, *26*, 1437.

[13] Marcher, B., Chapoy, L., & Christensen, D. H. (1988). *Macromolecules*, *21*, 677.

[14] Manickam, M., Kumar, S., Preece, J. A., & Spencer, N. (2000). *Liq. Cryst.*, *27*, 703.

[15] We have chosen the triphenylene mesogenic structure for several reasons: (i) they have pronounced photoconductivity (Simmerr, J., Glüsen, B., Paulus, W., Kettner, A., Schumacher, P., Adam, D., Etzbach, K. H., Siemeseyer, K., Wendorf, J. H., Ringsdorf, H., & Haarer, D. (1996). *Adv. Mater.*, *8*, 815), (ii) they have a strong tendency to form columnar mesophases (Chandresekhar, S. & Kumar, S. (1997). *Science Spectra*, *8*, 66; Allen, M. T., Diele, S., Harris, K. D. M., Hegmann, T., Kumari, N., Kariuki, B. M., Lose, D., Preece, J. A., & Tschierske, C. (2000). *Liq. Cryst.*, *27*, 689), and it is well recognised that the supramolecular structure of disc-shaped molecules, in general, is well suited for the one dimensional charge migration (see Markovitski, D., Marguet, S., Gallos, L. K., Sigal, H., Millie, P., Argyrakis, P., Ringsdorf, H., & Kumar, S. (1999). *Chem. Phys. Lett.*, *306*, 163) and one dimensional chain migration (see Boden, N., Borner, R. C., Bushby, R. J., & Clements J. (1994). *J. Am. Chem. Soc.*, *116*, 10807; Balagurusamy, V. S. K., Krishna Prasad, S., Chandrasekhar, S., Kumar, S., Manickam, M., & Yelamaggad, C. V. (1999). *Pramana*, *53*, 3) as well as ferroelectrical properties (see, Bock, H. & Helfrich, W. (1995). *Liq. Cryst.*, *18*, 387), optoelectrical switching behaviour (Lin, C. Y., Pan, H. L., Fox, M. A., & Bard, A. J. (1993). *Science*, *261*, 897), and photovoltaic behaviour (Greg, B. A., Foc, M. A., & Bard, A. J. (1990). *J. Phys. Chem.*, *94*, 1586), and (iii) doping with TNF can induce liquid crystalline behaviour in many triphenylene materials that initially do not show mesophase properties, Kranig, W., Boefield, C., & Spiess, H. W. (1990). *Liq. Cryst.*, *8*, 375; Bengs, H., Karthaus, O., Ringsdorf, H., Baehr, C., Ebert, M., & Wendorf, J. H. (1999). *Liq. Cryst.*, *10*, 161.

[16] a) Manickam, M., Kumar, S., Preece, J. A., & Spencer, N. (2000). *Liquid Crystals*, *27*, 703–706.
(b) Manickam, M., Belloni, M., Varshney, S. K., Shankar Rao, D. S., Ashton, P. R., Kumar, S., Preece, J. A., & Spencer, N. (2001). *J. Mater. Chem.*, *11*, 2790–2800.

[17] a) Markovitski, D., Pfeffen, N., Charra, F., Nunzi, J.-M., Bengs, H., & Ringsdorf, H. (1993). *J. Chem. Soc. Faraday Trans.*, *89*, 37.
b) Boden, N., Bushby, R. J., & Hubbard, J. F. (1997). *Mol. Cryst Liq. Cryst.*, *304*, 195.
c) Stracke, A., Wendorf, J. H., Janietz, D., & Mahlstedt, S. (1999). *Adv. Mater.*, *11*, 667.
d) Praefcke, K. & Singer, D. (1998). In: "*Handbook of Liquid Crystals*", Demus, D., Gray, G. W., Spiess, H. W., & Vill, V. (Eds.), Vol. 2B, 943–967.

[18] a) Kumar, S. & Manickam, M. (1998). *Synthesis*, 1119; b) Kumar, S. & Manickam, M. (1998). *Chem. Comm.*, 1427.

[19] a) Belloni, M., Manickam, M., Ashton, P. R., Preece, J. A., Spencer, N., & Wilkie, J. (2001). *Mol. Cryst. Liq. Cryst.*, *369*, 17–35.
b) Belloni, M., Manickam, M., & Preece, J. A. (2002). *Ferroelectrics*, *276*, 103–126.

[20] Cooke, G., Rahdi, A., Boden, N., Bushby, R. J., Lu, Z., Brown, S., & Heath, S. L. (2000). *Tetrahedron*, *56*, 3385–3390.

[21] Cooke, G., Kaushal, N., Boden, N., Bushby, R. J., Lu, Z., Brown, S., & Lozman, O. (2000). *Tett. Lett.*, *41*, 7955–7959.

[22] Bechgaard, K. & Parker, V. D. (1972). *J. Am. Chem. Soc.*, *94*, 4749.

[23] a) Singer, D., Liebman, A., Praefcke, K., & Wendorf, J. H. (1993). *Liq. Cryst.*, *14*, 785.
b) Ringsdorf, H., Wusterfeld, R., Zerta, E., Ebert, M., & Wendorf, J. H. (1989). *Angew. Chem. Int. Ed. Engl.*, *28*, 914.

[24] a) Boden, N., Bushby, R. J., Cooke, G., Lozman, O. R., & Lu, Z. (2001). ***J. Am. Chem. Soc.***, ***123***, 7915–7916.
b) Boden, N., Bushby, R. J., Liu, Q., & Lozman, O. R. (2001). ***J. Mat. Chem.***, ***11***, 1612–1617.