Preparation of Novel Banana-Shaped Triple Helical Liquid Crystals by Metal Coordination

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Abstract: The synthesis of a series of banana-shaped structures has been carried out, in which the bend unit is formed by a 4,4’-methyleneedianiline or 3,3’-methyleneedianiline core bearing two symmetric pyridylimine linkages to di- and tri- alkoxyphenylester moieties on the side arms. The molecules, in addition to providing an elongated aromatic central core associated with liquid crystal (LC) molecules, also provide binding sites for metals. The methylenedianiline spacer incorporates phenylene groups that sterically prevent the two binding sites from co-ordinating to a single metal centre and the central methylene unit introduces enhanced flexibility into the ligand backbone. Furthermore, complexes have been formed by the co-ordination between 3, 3’-methylenedianiline containing ligands and Cu (I) ions [Cu₂(3a-c)₂][PF₆]₂. Electrospray Mass Spectrometry (ESMS) and Fast Atom Bombardment Mass Spectrometry (FABMS) showed the formation of dimeric species; [Cu (L)]₂[PF₆]₂. Finally, thermal analysis of the ligands (1a-d, 2a-d, 3a-c and 4a-d) and Cu complexes [Cu₂(3a-c)₂][PF₆]₂ has been carried out in order to investigate the phase properties of these materials. None of the banana-shaped ligands and the metal complexes [Cu₂(3a-c)₂][PF₆]₂ showed any mesophases.
Keywords: Metallomesogens; banana; liquid crystals; triple helical; mesogenic.

1. Introduction

Although classical thermotropic liquid crystals (LCs) are commonly composed of rod-like molecules, many liquid crystals exhibit unconventional molecular structures. An example of such a molecular architecture is a banana-shaped one, with a bend in the middle of the mesogenic part [1-4]. Niori et al. [5] first observed ferroelectricity in a smectic phase which was produced from achiral banana-shaped molecules. Since then, several other research groups have [6] reported banana-shaped molecules that exhibited ferroelectric properties in the mesophase. The ferroelectricity is attributed to the polar packing of molecules with C2v symmetry where the molecules are packed in the same direction. A great many analogous banana-shaped structures have been prepared, some with lateral substituents in the central aromatic ring, which exhibit the wide range of ‘banana phases’ commonly designated B1 through to B7 [7]. The existence of such mesophases depends on the length of the rigid core, as well as on the magnitude of the bend angle and its position. The structure and flexibility of the angled segment are also important [8].

Dating back to the 1980s there has been immense interest in metal-containing mesogens, and subsequently a novel subfield in liquid crystals has emerged, known as metallomesogens. One of the factors contributing to this growth of interest has been due to the presence of the metal atom causing significant change in the magnetic, electric and optical properties of liquid crystals [9-11]. Many liquid crystals calamites based on rare earth element complexes [9] have exhibited enhance magnetic susceptibility among liquid crystals, for example Dy and Tb complexes with Schiff’s bases and β-aminovinyl ketones demonstrate high anisotropies of magnetic susceptibility [9]. At present, the molecular motifs of the known metallomesogens are based on the classical rod-like [12-15] and disc-shaped mesogens [16]. One of the modern pioneers in this field is Bruce et al., who has demonstrated [12-15] that by a suitable choice of anisotropic ligand, it is possible to form rod-like liquid crystals based on the metals with octahedral coordination geometry [12,13]. Strong chelating moieties such as 2,2'-bipyridine [12] and imine [13] moieties have been utilised as the metal chelating units in these metallomesogens. Also, Ziesel et al., have prepared several ligands based on 2,2'-bipyridine and these ligands assembled into a dinuclear double-helicate complex with copper that exhibits columnar mesophase [17].

Hannon et al. [18,19] have shown that bispyridylimine ligands can form double or triple stranded helicate structures. The triple helicate arises through the entwining of three bispyridylimine ligand strands around two metal cations, while the double helicates arise with tetrahedral metal ions. Herein, two novel series of banana-shaped molecules have been prepared that incorporate metal binding units (Scheme 1). The binding units contain 4,4’-methylenedianiline and 3,3’-methylenedianiline moieties as the central units which are linked to pyridine-2-carbaldehyde, affording imine structures. It is envisaged from the chemistry of the unsubstituted analogues (X-ray structures of their complexes are known [18,19,20]) that the helicates formed from the 4,4’-methylenedianiline core will form gross linear structures [18,21] and hence chemical modification at the terminal of this helicate with alkyl chains will result in classical rod-like mesogenic structures. Whereas, the helicates formed from the
3,3′-methylenedianiline which is structurally constrained will develop a kink at the centre of the helicate [20] and thus, with alkyl chains at the terminal of the helicate will form novel banana mesogenic structures [Cu₂(3a-c)₂][PF₆]₂. The thermal properties of these ligands (1a-d, 2a-d, 3a-c and 4a-d) and complexes [Cu₂(3a-c)₂][PF₆]₂ have been investigated.

Scheme 1. Desired banana-shaped molecules and the preparation of Cu complexes.

2. Results and Discussion

2.1. Design

The exact relationship between angled molecular structures and liquid crystalline properties is still not very clear to date, but empirical rules about molecular design [22-27] have shown that this new class of banana mesogen is extremely sensitive to structural modification regarding the attainment of mesophases. For example, flexibility [22,28], bend angle [7,28], nature of the central core [22,29-31], length [26,31] and nature [32] of the terminal chains, substituents both on the central [7,26], and on the side arms [33], dipoles [26], and direction of linking groups [34] are among the main variants contributing to the capability of a material to exhibit liquid crystalline properties.
Here a synthetic scheme has been devised that allows the incorporation of 4,4'-methylenedianiline and 3,3’-methylenedianiline units as the central core of the molecular architecture, which as well as providing the bent core for the banana-shaped molecules, provide pyridylimine and methylene dianiline units for binding to metal ions.

2.2. Synthesis

The syntheses of the novel banana-shaped compounds (1a-d, 2a-d, 3a-c and 4a-d) were achieved via a series of reactions as illustrated in Scheme 2. The commercially available di- and trihydroxy benzoic acids 6 and 7 were converted to their respective methyl esters in the presence of a catalytic amount of concentrated H$_2$SO$_4$ in MeOH to afford compounds 8 and 9. Alkylation of compounds 8 and 9 was achieved under basic conditions (K$_2$CO$_3$) with n-bromopentane, n-bromoheptane, n-bromononane and n-bromododecane, respectively affording compounds 10a-d and 11a-d [13]. The esters 10a-d and 11a-d were hydrolysed to the corresponding acids 12a-d and 13a-d under basic conditions (NaOH) [13]. The commercially available 5-hydroxy-2-methylpyridine (14) was directly oxidised with H$_2$O$_2$ to afford the N-oxide 15. The N-oxide was subsequently heated in acetic anhydride to afford the acetate 16. Under acidic conditions (concentrated HCl) compound 16 was deprotected to afford the alcohol 17. Selective oxidation of the alcohol moiety was achieved in the presence of a mild oxidising agent, MnO$_2$ [35], to afford compound 18. Compound 18 was then coupled with the acids 12a-d and 13a-d through dicyclohexylcarbodiimide (DCC) [13] coupling to afford the respective aldehydes 19a-d and 20a-d. The target imine compounds 1a-d, 2a-d, 3a-c and 4a-d were obtained via stirring under N$_2$ atmosphere at room temperature between the respective aldehydes 19a-d and 20a-d and methylene dianilines [36]. Finally, the complexes [Cu$_2$(3a-c)$_2$][PF$_6$]$_2$ were formed by coordination of molecules 3a-c to Cu (I) ions at room temperature in iso-PrOH [18,21].

2.3. Thermal Properties of Bent-shaped Ligands

Thermal analysis was carried out on compounds 1a-d, 2a-d, 3a-c and 4a-d using variable temperature optical polarised microscope (OPM) between crossed polarisers, and differential scanning calorimetry (DSC). OPM revealed that upon heating from solid to the liquid phase, no birefringent liquids were formed, and the materials passed straight to the isotropic liquid phase. On cooling the I→K transition was observed at slightly lower temperatures, confirming the lack of any mesophase formation. However, for a few of the compounds (2a, 4c-d) the I→K transition was not observed. This result suggests that these compounds decomposed through the K→I transition. As expected, for all the 1a-d, 2a, 2d, 4c and 4d derivatives, the K→I transition decreased with increasing the length of the carbon chain. The DSC traces are illustrated in Figure 1 and the melting points are listed in Table 1.
Scheme 2. Synthesis of the desired banana-shaped molecules

(i): Conc. H₂SO₄, MeOH, reflux, 20 hrs; (ii): n-bromoalkane, K₂CO₃, MeCN, reflux, 20 hrs; (iii): NaOH (aq), MeOH, reflux, 20 hrs; (iv): H₂O₂, AcOH, 80 °C, 3 hrs, then stir at rt, 24 hrs; (v): (CH₃CO)₂O, 140 °C, 2 hrs; (vi): Conc. HCl, reflux, 1.5 hrs; (vii): MnO₂, iPrOH, reflux, 4 hrs; (viii): EDC, 4-DMAP, dried DCM, stirred at r.t, 24 hrs; (ix): anhydrous EtOH, stirred at 50 °C, 24 hrs.
**Figure 1.** DSC traces for compounds **1a, 1d, 2a, 2d, 4c and 4d** (second heating cycle at a rate of 5 °C/min).

1a: $R = C_5H_{11}$

1d: $R = \ldots$

2a: $R = C_5H_{11}$

2d: $R = \ldots$

4c: $R = C_9H_{19}$

4d: $R = C_{12}H_{25}$
Table 1. Transition temperatures (onset values) (°C) and enthalpy values $\Delta H$ (kJ/mol) recorded on second heating by DSC (10 °C/min) for compounds 1a-d, 2a, 2d, 4c and 4d.

| Entry | K→I | $\Delta H$ |
|-------|-----|------------|
| 1a    | 158 | 81.3       |
| 1b    | 136 | 64.3       |
| 1c    | 129 | 40.0       |
| 1d    | 126 | 81.0       |
| 2a    | 67  | 43.7       |
| 2d    | 51  | 115.8      |
| 4c    | 51  | 60.8       |
| 4d    | 55  | 85.4       |

2.4. Metal Complexes

Cu complexes $[\text{Cu}_2(3a-c)_2][\text{PF}_6]_2$ were isolated as red precipitates and through UV/vis spectroscopy $\lambda_{max}$ are determined as 495, 485 and 480 nm, respectively, which are characteristic for Cu (I) ions in a bis-pyridylimine environment [18,20,21]. The masses obtained for complexes $[\text{Cu}_2(3a)_2][\text{PF}_6]_2$ and $[\text{Cu}_2(3b)_2][\text{PF}_6]_2$ from ES and FAB mass spectrometry, show that the species formed are dinuclear double stranded arrays in the form of $[\text{Cu}_2(3a-c)_2][\text{PF}_6]_2$. In the case of $[\text{Cu}_2(3c)_2][\text{PF}_6]_2$, the sample did not fly in the ESMS. $^1$H-NMR spectra recorded in CD$_2$Cl$_2$ for $[\text{Cu}_2(3a-c)_2][\text{PF}_6]_2$, all show broad peaks in the aromatic region suggesting that more than one species is present. As previously described [18,20,21] these dinuclear double stranded arrays can exist as helicate (rac-isomer) and box (meso-isomer) and these two are commonly interchanging in the NMR timescale leading to broad NMR peaks. The meso-isomer is usually the enthalpic product (the dominant solid state species) while the helicate is favoured entropically and is the major product in solution at room temperature [18,20,21]. In particular, $[\text{Cu}_2(3c)_2][\text{PF}_6]_2$, the NMR peaks were extremely broad making peak assignments difficult.

Liquid crystal properties of these free ligands 1a-d, 2a-d, 3a-c, and 4a-d and the three copper Cu (I) complexes $[\text{Cu}_2(3a-c)_2][\text{PF}_6]_2$ were investigated using an OPM. Unfortunately, none of the compounds exhibited liquid crystalline phases. Possible reasons for this could lie in the ligands having too much flexibility about the central methylene unit. Secondly the two isomeric forms of the copper (I) complexes may prevent the molecules from becoming sufficiently ordered in the mesophase.

3. Experimental

3.1. General

The starting materials which were commercially available were purchased from Aldrich and used as received. The solvents were purchased from Fisher Scientific (CH$_2$Cl$_2$, EtOAc, Et$_2$O and MeOH) or Aldrich (anhydrous EtOH). Solvents were either used as received or dried; DCM was distilled from CaCl$_2$ under a N$_2$ atmosphere. Yields refer to chromatographically pure products. Thin-layer
chromatography (TLC) was carried out on aluminum sheets coated with silica gel 60 (Merck 5554 mesh). Column chromatography was performed on silica gel 60 (Merck 230-400). Microanalyses were performed by the University of London microanalytical laboratories or by the University of Birmingham microanalytical services. Electron impact (EI) mass spectra were recorded at 70eV on a VG ProSpec mass spectrometer. Liquid secondary ion mass spectra (LSIMS) were recorded on a VG ZabSpec mass spectrometer equipped with a cesium ion source and utilizing m-nitrobenzyl alcohol containing a trace of sodium acetate as the liquid matrix. 1H-NMR spectra were recorded on a Bruker AC 300 (75.5 MHz) spectrometer. The chemical shift values are expressed as δ values and the coupling constant values (J) are in Hertz (Hz). The following abbreviations are used for the signal multiplicities or characteristics: s, singlet; d, doublet; dd, doublet of doublets; t, triplet; m, multiplet; 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 microscope as well as differential scanning calorimetry (DSC7 Perkin-Elmer).

**Methyl 3,4-dihydroxybenzoate (8):** A solution of 3,4-dihydroxybenzoic acid (6, 15.00 g, 97.30 mmol) and conc. H2SO4 (1.5 mL) in MeOH (200 mL) was stirred and heated under reflux overnight. The resultant yellow solution was allowed to cool to room temperature and the solvent removed in vacuo, affording a brown solid (14.60 g, 82%). mp: 126-129 °C; 1H-NMR (acetone-d6): δH 8.55 (br s, 1H, OH), 7.50 (d, J = 2.0 Hz, 1H, Ar-H), 7.44 (dd, 1H, Ar-H, J = 8.3, 2.0 Hz), 6.90 (d, 1H, Ar-H, J = 8.3 Hz.), 3.80 (s, 3H, OMe), 3.01 (br s, 1H, OH); 13C-NMR (acetone-d6): δC 167.0, 150.7, 145.5, 123.2, 122.7, 117.0, 115.7, 51.8; MS m/z (EIMS): 168 ([M] +, 54%), 137 ([M-OMe] +, 100%), 109 ([M-CO2Me] +, 20%); IR v/cm⁻¹ (nujol): 3468, 3263, 2927, 2854, 1690.

**Methyl 3,4,5-trihydroxybenzoate (9):** The same procedure as described for the preparation of 8 was followed, using 3,4,5-trihydroxybenzoic acid (7, 16.60 g, 97.40 mmol), conc. H2SO4 (0.5 mL) and MeOH (200 mL). This yielded a pale brown solid (14.40 g, 80%). mp: 120-124 °C; 1H-NMR (acetone-d6): δH 7.11 (s, 2H, Ar-H), 3.78 (s, 3H, OMe); 13C-NMR (acetone-d6): δC 167.9, 146.7, 139.5, 122.5, 110.5, 49.3; MS m/z (EIMS): 184 ([M] +, 55%), 153 ([M-OMe] +, 100%), 125 ([M-CO2Me] +, 17%); IR v/cm⁻¹ (nujol): 3468, 3263, 1690.

**Methyl 3,4-dipentyloxybenzoate (10a):** A suspension of K2CO3 (9.90 g, 71.63 mmol) in a solution of methyl 3,4-dihydroxybenzoate (8, 3.00 g, 17.84 mmol) and n-bromopentane (6.75 g, 44.69 mmol) in MeCN (100 mL) was stirred and heated under reflux overnight. The resultant brown mixture was allowed to cool to room temperature and concentrated in vacuo (30 mL). Water (250 mL) was added and the aqueous layer was extracted by washing with Et2O (3 x 100 mL). The combined organic layers were washed with brine solution (50 mL), dried (MgSO4), filtered and solvent removed in vacuo, yielding an orange oil as the crude product. The crude product was purified via silica gel column chromatography (gradient elution: 0 to 10 % EtOAc in hexane, increase polarity in increments of 5% per 150 mL of eluent used). The solvent was removed in vacuo to yield a colourless oil (4.84 g, 88%). 1H-NMR (CDCl3): δH 7.62 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.53 (d, 1H, Ar-H, J = 2.2 Hz), 6.86 (d, 1H, Ar-H, J = 8.5 Hz), 4.05-4.02 (m, 4H, 2 x OCH2), 3.88 (s, 3H, OMe), 1.89-1.79 (m, 4H, 2 x CH2),
1.50-1.33 (m, 8H, 4 x CH₂), 0.87 (t, 6H, 2 x CH₃, J = 7.0Hz); ¹³C-NMR (CDCl₃): δc 167.0, 153.1, 148.4, 123.5, 122.4, 114.1, 111.9, 69.2, 69.0, 51.9, 28.9, 28.2, 22.5, 14.1; MS m/z (EIMS): 308 ([M]+, 28 %), 168 ([M-(2 x C₅H₁₀)]⁺, 24%); IR v/cm⁻¹ (nujol): 2926, 2856, 1718.

Using the same general procedure as described for 10a, the following compounds were prepared:

**Methyl 3,4-diheptyloxybenzoate (10b):** From K₂CO₃ (9.90 g, 71.63 mmol) methyl 3,4-dihydroxybenzoate (8, 3.00 g, 17.84 mmol) and n-bromoheptane (8.10 g, 45.23 mmol). This yielded a pale yellow oil (6.00 g, 92%). mp: 30-32 °C; ¹H-NMR (CDCl₃): δH 7.63 (dd, 1H, Ar-H, J = 8.5, 2.0 Hz), 7.53 (d, 1H, Ar-H, J = 2.0 Hz), 6.85 (d, 1H, Ar-H, J = 8.5 Hz), 4.04-4.03 (m, 4H, 2 x OCH₂), 3.88 (s, 3H, OMe), 1.85-1.80 (m, 4H, 2 x CH₂), 1.31-1.25 (m, 4H, 2 x CH₂); ¹³C-NMR (CDCl₃): δc 167.2, 153.3, 148.6, 123.7, 122.5, 114.3, 112.0, 69.4, 69.1, 52.1, 32.0, 29.2, 29.1; MS m/z (EIMS): 365 ([M+H]+, 100%); IR ν/cm⁻¹ (nujol): 2926, 2856, 1723.

**Methyl 3,4-dinonyloxybenzoate (10c):** From K₂CO₃ (9.90 g, 71.63 mmol), methyl 3,4-dihydroxybenzoate (8, 3.00 g, 17.84 mmol) and n-bromononane (9.26 g, 44.70 mmol). This yielded a white solid (6.64 g, 88%). mp: 36-38 °C; ¹H-NMR (CDCl₃): δH 7.62 (dd, 1H, Ar-H, J = 8.5, 2.0 Hz), 7.52 (d, 1H, Ar-H, J = 2.0 Hz), 6.85 (d, 1H, Ar-H, J = 8.5 Hz), 4.05-4.03 (m, 4H, 2 x OCH₂), 3.87 (s, 3H, OMe), 1.88-1.76 (m, 4H, 2 x CH₂), 1.46-1.25 (m, 24H, 12 x CH₂), 0.87 (t, 6H, 2 x CH₃, J = 6.6 Hz); ¹³C-NMR (CDCl₃): δc 167.0, 153.2, 148.5, 123.5, 122.4, 114.2, 111.9, 69.3, 69.0, 51.9, 31.9, 29.6, 29.4, 29.3, 29.1, 26.0, 22.8, 14.2; MS m/z (EIMS): 420 ([M]+, 46%), 154 ([M-(2 x C₇H₁₄)]⁺, 100%); IR ν/cm⁻¹ (nujol): 2927, 2853, 1723.

**Methyl 3,4-didodecanyloxybenzoate (10d):** From K₂CO₃ (9.90 g, 71.63 mmol), methyl 3,4-dihydroxybenzoate (8, 3.00 g, 17.84 mmol) and n-bromododecane (11.12 g, 44.62 mmol). This yielded a white solid (6.81 g, 76%). mp: 46-48 °C; ¹H-NMR (CDCl₃): δH 7.62 (dd, 1H, Ar-H, J = 8.5, 2.0 Hz), 7.52 (d, 1H, Ar-H, J = 2.0 Hz), 6.85 (d, 1H, Ar-H, J = 8.5 Hz), 4.05-4.03 (m, 4H, 2 x OCH₂), 3.87 (s, 3H, OMe), 1.88-1.79 (m, 4H, 2 x CH₂), 1.47-1.27 (m, 36H, 18 x CH₂), 0.87 (t, 6H, 2 x CH₃, J = 6.6 Hz); ¹³C-NMR (CDCl₃): δc 167.0, 153.2, 148.5, 123.5, 122.4, 114.2, 111.9, 69.3, 69.0, 51.9, 31.9, 29.7, 29.4, 29.2, 29.1, 26.0, 22.7, 14.2; MS m/z (EIMS): 505 ([M+H]+, 100%); IR ν/cm⁻¹ (nujol): 2926, 2855, 1718.

**Methyl 3,4,5-tripentyloxybenzoate (11a):** From methyl 3,4,5-trihydroxybenzoate (9, 3.83 g, 20.83 mmol) and n-bromopentane (11.01 g, 72.91 mmol), K₂CO₃ (11.50 g, 83.3 mmol) and MeCN (100 mL). This yielded a pale yellow oil (5.07 g, 61%). ¹H-NMR (CDCl₃): δH 7.24 (s, 2H, Ar-H), 4.01 (t, 6H, 3 x OCH₂, J = 6.6 Hz), 3.88 (s, 3H, OMe), 1.86-1.69 (m, 6H, 3 x CH₂), 1.48-1.32 (m, 12H, 6 x CH₂), 0.92 (t, J = 7.0 Hz, 3H, CH₃), 0.91 (t, 6H, 2 x CH₃, J = 7.0 Hz); ¹³C-NMR (CDCl₃): δc 165.4, 151.3, 140.9, 123.0, 106.5, 71.9, 67.6, 50.5, 28.4, 27.4, 26.7, 21.0, 20.9, 12.5; MS m/z (EIMS): 394 ([M]+, 20%), 324 ([M-C₅H₁₀]⁺, 5%), 184 ([M-(3 x C₅H₁₀)]⁺, 100%); IR ν/cm⁻¹ (nujol): 2925, 2854, 1718.
Methyl 3,4,5-triheptyloxybenzoate (11b): From K$_2$CO$_3$ (9.90 g, 71.63 mmol) methyl 3,4,5-trihydroxybenzoate (9, 3.83 g, 20.82 mmol) and n-bromoheptane (13.04 g, 72.85 mmol). This yielded a yellow oil (5.97 g, 60%). $^1$H-NMR (CDCl$_3$): $\delta$H 7.24 (s, 2H, Ar-H), 4.00 (t, 6H, 3 x OCH$_2$, $J = 6.6$ Hz), 3.88 (s, 3H, OMe), 1.85-1.68 (m, 6H, 3 x CH$_2$), 1.48-1.29 (m, 24H, 12 x CH$_2$), 0.88 (t, 9H, 3 x CH$_3$, $J = 7.0$ Hz); $^{13}$C-NMR (CDCl$_3$): $\delta$C 165.1, 151.0, 140.8, 122.9, 106.2, 71.6, 67.3, 50.2, 30.0, 28.5, 27.5, 27.3, 27.2, 24.2, 20.8, 12.2; MS m/z (EIMS): 478 ([M]$^+$, 72 %), 380 ([M-C$_7$H$_{14}$]$^+$, 25%), 184 ([M-(3 x C$_7$H$_{14}$)]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2930, 2870, 1723.

Methyl 3,4,5-trinonyloxybenzoate (11c): From K$_2$CO$_3$ (9.90 g, 71.63 mmol) methyl 3,4,5-trihydroxybenzoate (9, 3.83 g, 20.82 mmol) and n-bromononane (15.08 g, 72.85 mmol). This yielded a yellow oil (7.37 g, 63%). $^1$H-NMR (CDCl$_3$): $\delta$H 7.24 (s, 2H, Ar-H), 4.00 (t, 6H, 3 x OCH$_2$, $J = 6.6$ Hz), 3.88 (s, 3H, OMe), 1.85-1.68 (m, 6H, 3 x CH$_2$), 1.48-1.27 (m, 18 x CH$_2$), 0.88 (t, 9H, 3 x CH$_3$, $J = 7.0$ Hz); $^{13}$C-NMR (CDCl$_3$): $\delta$C 165.8, 151.3, 140.9, 122.9, 106.8, 71.9, 67.7, 54.1, 33.9, 32.3, 31.6, 31.4, 31.3, 28.1, 24.7, 16.1; MS m/z (ESMS): 585 ([M+Na]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2930, 2871, 1723.

Methyl 3,4,5-tridodecyloxybenzoate (11d): From K$_2$CO$_3$ (9.90 g, 71.63 mmol) methyl 3,4,5-trihydroxybenzoate (9, 3.83 g, 20.82 mmol) and n-bromododecane (18.14 g, 72.85 mmol). This yielded a yellow oil (9.02 g, 63%). $^1$H-NMR (CDCl$_3$): $\delta$H 7.24 (s, 2H, Ar-H), 4.00 (t, 6H, 3 x OCH$_2$, $J = 6.6$ Hz), 3.88 (s, 3H, OMe), 1.85-1.68 (m, 6H, 3 x CH$_2$), 1.48-1.29 (m, 27 x CH$_2$), 0.88 (t, 9H, 3 x CH$_3$, $J = 6.99$ Hz); $^{13}$C-NMR (CDCl$_3$): $\delta$C 166.2, 152.0, 141.2, 123.1, 107.2, 72.6, 68.3, 51.0, 31.0, 29.4, 28.2, 28.4, 28.1, 25.0, 21.8, 13.2; MS m/z (ESMS): 688 ([M+Na]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2930, 2870, 1723.

3,4-Dipentyloxybenzoic acid (12a): To a solution of methyl 3,4-dipentyloxybenzoate (10a, 4.84 g, 15.7 mmol) in MeOH (150 mL), an aqueous solution of sodium hydroxide (15 mL, 2.10 mol L$^{-1}$) was added and the mixture was stirred and heated under reflux overnight. The resultant colourless solution was allowed to cool to room temperature and HCl (2 M) was added dropwise to acidify the solution, whereupon a white precipitate was formed, which was filtered off. The filtrate was concentrated in vacuo (~20 mL) and water (100 mL) was added. The aqueous layer was extracted with Et$_2$OAc (3 x 100 mL). The combined organic layers were washed with brine solution (20 mL), dried (MgSO$_4$) and filtered. The solvent was removed in vacuo, yielding a white solid (4.00 g, 87%). mp: 126-128 °C; $^1$H-NMR (CDCl$_3$): $\delta$H 7.24 (s, 2H, Ar-H), 7.58 (d, 1H, Ar-H, $J = 2.2$ Hz), 6.89 (d, 1H, Ar-H, $J = 8.5$ Hz), 4.07-4.04 (m, 4H, 2 x OCH$_2$), 1.88-1.82 (m, 8H, 4 x CH$_2$), 0.87 (t, 6H, 2 x CH$_3$, $J = 6.6$ Hz); $^{13}$C-NMR (CDCl$_3$): $\delta$C 171.7, 153.9, 148.5, 124.5, 121.4, 144.5, 111.8, 69.3, 69.0, 28.7, 28.2, 22.5, 14.1; MS m/z (EIMS): 294 ([M]$^+$, 25%), 224 ([M-C$_5$H$_{10}$]$^+$, 9%), 154 ([M-(2 x C$_6$H$_{10}$)]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2926, 2856, 2646, 1848.

Following the same general procedure described for 12a, the following compounds were prepared:

3,4-Diheptyloxybenzoic acid (12b): From compound 11b (5.94 g, 16.30 mmol) and sodium hydroxide (15 mL, 2.18 mol L$^{-1}$). This yielded a white solid (4.70 g, 82%). mp: 120-123 °C; $^1$H-NMR (CDCl$_3$): $\delta$H 7.70 (dd, 1H, Ar-H, $J = 8.5, 2.2$ Hz), 7.56 (d, 1H, Ar-H, $J = 2.2$ Hz), 6.87 (d, 1H, Ar-H, $J = 8.5$ Hz),
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4.05-4.02 (m, 4H, 2 x OCH2), 1.83-1.81 (m, 4H, 2 x CH2), 1.31-1.25 (m, 16H, 8 x CH2), 0.88 (t, 6H, 2 x CH3, J = 6.6 Hz); 13C-NMR (CDCl3): δC 171.9, 153.7, 148.3, 124.3, 121.3, 114.3, 111.6, 69.1, 68.8, 31.0, 28.9, 25.8, 22.8, 13.9; MS m/z (EIMS): 351 ([M+H]+, 25%), 333 ([M-OH]+, 100%); IR ν/cm⁻¹ (nujol): 2925, 2855, 2646, 1670s.

3,4-Dinonyloxybenzoic acid (12c): From compound 10c (6.42 g, 15.26 mmol) and sodium hydroxide (15 mL, 2.03 mol L⁻¹). This yielded a white solid (5.85 g, 94%). mp: 112-114 °C; 1H-NMR (CDCl3): δH 7.71 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.52 (d, 1H, Ar-H, J = 2.2 Hz), 6.85 (d, 1H, Ar-H, J = 8.5 Hz), 4.07-4.03 (m, 4H, 2 x OCH2), 1.87–1.79 (m, 4H, 2 x CH2), 1.49–1.27 (m, 24H, 12 x CH2), 0.87 (t, 6H, 2 x CH3, J = 6.6 Hz); 13C-NMR (CDCl3): δC 172.0, 154.1, 148.7, 124.7, 121.5, 114.6, 112.0, 69.4, 69.2, 32.1, 29.7, 29.6, 26.5, 26.2, 22.9, 14.3; MS m/z (EIMS): 406 ([M]+, 46%), 280 ([M-C7H14]+, 154%); IR ν/cm⁻¹ (nujol): 2926, 2854, 2644, 1670.

3,4-Didodecanyloxybenzoic acid (12d): From compound 10d (6.55 g, 12.98 mmol) and sodium hydroxide (15 mL, 1.87 mol L⁻¹). This yielded a white solid (5.64 g, 89%). mp: 106-109 °C; 1H-NMR (CDCl3): δH 7.71 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.57 (d, 1H, Ar-H, J = 2.2 Hz), 6.88 (d, 1H, Ar-H, J = 8.5 Hz), 4.07-4.03 (m, 4H, 2 x OCH2), 1.87-1.79 (m, 4H, 2 x CH2), 1.52-1.26 (m, 36H, 18 x CH2), 0.87 (t, 6H, 2 x CH3, J = 6.6 Hz); 13C-NMR (CDCl3): δC 172.1, 154.3, 148.8, 124.9, 121.6, 114.7, 112.1, 69.6, 69.4, 32.3, 29.9, 29.8, 26.5, 26.4, 26.2, 25.6, 22.9, 14.5; MS m/z (ESMS): 513 ([M+Na]+, 100%); IR ν/cm⁻¹ (nujol): 2926, 2854, 2644, 1670.

3,4,5-Tripentyloxybenzoic acid (13a): From compound 11a (4.62 g, 11.73 mmol) and sodium hydroxide (15 mL, 2.18 mol L⁻¹). This yielded a white solid (4.46 g, 74%). mp: 48-50 °C; 1H-NMR (CDCl3): δH 7.12 (s, 2H, Ar-H), 3.89 (t, 2H, OCH2, J = 6.4 Hz), 3.79 (t, 4H, 2 x OCH2, J = 5.9 Hz), 1.61-1.69 (m, 6H, 3 x CH2), 1.42-1.25 (m, 12H, 6 x CH2), 0.89 (t, 3H, CH3, J = 7.0 Hz), 0.85 (t, 6H, 2 x CH3, J = 6.8 Hz); 13C-NMR (CDCl3): δC 173.4, 153.5, 142.7, 127.4, 108.9, 74.1, 69.7, 31.0, 30.1, 29.3, 29.2, 23.5, 14.9; MS m/z (EIMS): 380 ([M]+, 25%), 170 ([M-(3 x C5H11)]+, 100%); IR ν/cm⁻¹ (nujol): 2927, 2854, 2646, 1684.

3,4,5-Triheptyloxybenzoic acid (13b): From compound 11b (5.50 g, 11.51 mmol) and sodium hydroxide (15 mL, 2.18 mol L⁻¹). This yielded a white solid (4.02 g, 76%). mp: 47-49 °C; 1H-NMR (CDCl3): δH 7.31 (s, 2H, Ar-H), 4.03 (t, 2H, OCH2, J = 6.6 Hz), 4.01 (t, 4H, 2 x OCH2, J = 6.6 Hz), 1.86-1.70 (m, 6H, 3 x CH2), 1.52-1.29 (m, 24H, 12 x CH2), 0.88 (t, 9H, 3 x CH3, J = 6.6 Hz); 13C-NMR (CDCl3): δC 173.8, 153.5, 142.9, 127.6, 109.0, 74.3, 69.8, 329, 32.8, 31.4, 30.4, 30.2, 27.2, 27.0, 23.6, 15.0; MS m/z (ESMS): 487 ([M+Na]+, 100%); IR ν/cm⁻¹ (nujol): 2926, 2854, 2646, 1670.

3,4,5-Trinonyloxybenzoic acid (13c): From compound 11c (7.10 g, 12.63 mmol) and sodium hydroxide (15 mL, 1.68 mol dm⁻³). This yielded a white solid (5.40 g, 78%). mp: 47-49 °C; 1H-NMR (CDCl3): δH 7.30 (s, 2H, Ar-H), 4.03 (t, 2H, OCH2, J = 6.6 Hz), 4.01 (t, 4H, 2 x OCH2, J = 6.6 Hz), 1.86-1.69 (m, 6H, 3 x CH2), 1.47-1.27 (m, 36H, 18 x CH2), 0.87 (t, 9H, 3 x CH3, J = 6.6 Hz); 13C-NMR (CDCl3): δC
170.8, 150.8, 140.1, 121.6, 106.5, 71.5, 67.1, 29.8, 28.2, 27.6, 27.5, 27.3, 27.2, 24.0, 20.6, 12.0; MS m/z (ESMS): 547 ([M-H]-, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2928, 2855, 2647, 1670.

3,4,5-Tridodecyloxybenzoic acid (13d): From compound 11d (8.80 g, 12.79 mmol) and sodium hydroxide (15 mL, 1.71 mol L$^{-1}$). This yielded a white solid (6.71 g, 81%). mp: 47-49 $^\circ$C; $^1$H-NMR (CDCl$_3$): $\delta$H 7.30 (s, 2H, Ar-H), 4.03 (t, 2H, OCH$_2$, $J =$ 6.6 Hz), 4.01 (t, 4H, 2 x OCH$_2$, $J =$ 6.6 Hz), 1.86-1.69 (m, 6H, 3 x CH$_2$), 1.47-1.25 (m, 54H, 27 x CH$_2$), 0.87 (t, 9H, 3 x CH$_3$, $J =$ 6.6 Hz); $^{13}$C-NMR (CDCl$_3$): $\delta$C 171.3, 151.1, 141.1, 122.1, 106.8, 71.8, 67.4, 30.2, 28.6, 27.9, 27.6, 27.5, 24.3, 20.9, 12.3; MS m/z (ESMS): 697 ([M+Na]+, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2926, 2854, 1674s.

5-Hydroxy-2-methylpyridine N-oxide (15): A solution of 5-hydroxy-2-methylpyridine (14, 15.0 g, 0.14 mol) and hydrogen peroxide 27.5 % (33 mL, 0.27 mol) in CH$_3$CO$_2$H (300 mL) was heated at 80 $^\circ$C for 2.5 hrs. A colour change of solution was observed from orange to pale yellow. The solution was further stirred at room temperature for 24 hrs and concentrated in vacuo (50 mL). Acetone (400 mL) was added to force precipitation. The resulting pale yellow precipitate was collected by vacuum filtration (12.7 g, 74%). mp: 188.9-189.5 $^\circ$C (decomposes); $^1$H-NMR (CD$_3$OD): $\delta$H 7.93 (d, 1H, Py-H, $J =$ 2.2 Hz), 7.32 (d, 1H, Py-H, $J =$ 8.8 Hz), 7.03 (dd, 1H, Py-H, $J =$ 8.8, 2.2 Hz), 2.41 (s, 3H, CH$_3$); $^{13}$C-NMR (CD$_3$OD): $\delta$C 158.7, 144.3, 136.0, 130.6, 122.1, 19.1; MS m/z (EIMS): 125 ([M]$^+$, 50%), 109 ([M-O]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2924, 2854, 1840, 1612.

2-Pyridylmethanol acetate (16): 5-Hydroxy-2-methylpyridine N-oxide (15, 17.5 g, 0.14 mol) was slowly added to (CH$_3$CO)$_2$O (170 mL) at 110 $^\circ$C. The resultant dark brown reaction mixture was stirred for 2 hrs at 140 $^\circ$C. EtOH (400 mL) was added and the solution was concentrated in vacuo to yield brown oil. CHCl$_3$ (100 mL) was added and the solution was neutralised with saturated NaHCO$_3$. The organic layers were collected through washings with saturated NaHCO$_3$ (2 x 20 mL), dried (MgSO$_4$) and filtered. The solvent was removed in vacuo to yield a brown oil, which was further dried under high vacuum for 2 hrs (26.1 g, 89%). $^1$H-NMR (CDCl$_3$): $\delta$H 8.40 (d, 1H, Py-H, $J =$ 2.6 Hz), 7.49 (d, 1H, Py-H, $J =$ 8.5 Hz), 7.39 (dd, 1H, Py-H, $J =$ 8.5, 2.6 Hz), 5.21 (s, 2H, CH$_2$), 2.33 (s, 3H, CH$_3$), 2.15 (s, 3H, CH$_3$); $^{13}$C-NMR (CDCl$_3$): $\delta$C 170.7, 168.9, 152.9, 146.7, 143.0, 130.0, 122.5, 66.3, 22.2, 21.0; MS m/z (FABMS): 210 ([MH]$^+$, 100%); IR $\nu$/cm$^{-1}$ (nujol): 2923, 2854, 1747, 1582.

5-Hydroxy-2-hydroxymethylpyridine (17): A solution of 2-pyridylmethanol acetate (16) in conc. HCl (30 mL) was heated under reflux for 1.5 hrs. The reaction mixture was cooled to room temperature and concentrated in vacuo. CHCl$_3$ (200 mL) was added and the solution neutralised carefully with saturated NaHCO$_3$. The aqueous layers were collected through washings with saturated NaHCO$_3$ and concentrated in vacuo. The brown solid was triturated with MeOH (500 mL) and filtrates collected through filtration. The solvent was removed in vacuo yielding a brown solid (8.3 g, 98%). $^1$H-NMR (CDCl$_3$): $\delta$H 7.85 (d, 1H, Py-H, $J =$ 2.6 Hz), 7.18 (d, 1H, Py-H, $J =$ 8.5 Hz), 7.01 (dd, 1H, Py-H, $J =$ 8.5, 2.6 Hz), 4.51 (s, 2H, CH$_2$); $^{13}$C-NMR (CDCl$_3$): $\delta$C 163.5, 147.8, 141.5, 128.0, 124.8, 66.7; MS m/z (FABMS): 125 ([M+H]$^+$, 35%).
5-Hydroxypyridine 2-carbaldehyde (18): A suspension of 5-hydroxy-2-hydroxymethylpyridine (17, 2.50 g, 19.98 mmol) and activated MnO₂ (1.74 g, 19.98 mmol) in iso-PrOH (100 mL) was heated under reflux for 3 hrs. The hot mixture was filtered through Celite® and washed thoroughly with hot MeOH (400 mL). The solution was allowed to cool to room temperature and concentrated in vacuo, yielding a brown solid. The solid was absorbed onto silica and purified via short silica gel column chromatography (gradient elution: 0 to 5% methanol in CH₂Cl₂, increase polarity in increments of 2 % per 150 mL of eluent used). The solvent was removed in vacuo to yield a brown solid (1.41 g, 57%). mp: 223-225 °C (decomposes); ¹H-NMR (CD₃OD): δH 9.60 (s, 1H, CHO), 7.90 (d, 1H, Py-H, J = 2.2 Hz), 7.74 (d, 1H, Py-H, J = 8.8 Hz), 6.84 (dd, 1H, Py-H, J = 8.8, 2.2 Hz), ¹³C-NMR (CD₃OD): 193.0, 172.2, 146.5, 140.9, 130.2, 126.6; MS m/z (FABMS): 123 ([M]⁺, 50%), 109 ([M-CH₂]⁺, 27%), 95 ([M-CO]⁺, 100%); IR ν/cm⁻¹ (nujol): 2923, 2854, 1668, 1507.

3,4-Bisdipentyloxybenzoic acid 6-formylpyridin-3-ester (19a): To a solution of 5-hydroxypyridine-2-carbaldehyde (18, 0.50 g, 2.44 mmol) in dry CH₂Cl₂ (30 mL), cooled in an ice bath under a N₂ atmosphere, compound 12a (0.72 g, 2.44 mmol), 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC) (1.16 g, 60.55 mmol) and 4-dimethylaminopyridine (catalytical amount) were added. The solution was stirred at room temperature under a N₂ atmosphere for 24 hrs. HCl (50 mL, 1 mol dm⁻³) was added, which yielded a white solid. MeOH (10 mL) was added to dissolve the precipitate. The organic layers were collected through washings with CH₂Cl₂ (3 x 30 mL), dried (MgSO₄) and filtered. The solvent was removed in vacuo, to yield a brown solid. The solid was absorbed onto silica and purified via silica gel column chromatography (gradient elution: 0 to 10 % EtOAc in hexane, increase polarity in increments of 5% per 150 mL of eluent used). The solvent was removed in vacuo to yield a white solid (0.35 g, 36%); mp: 63-66 °C; ¹H-NMR (CDCl₃): δH 10.09 (s, 1H, CHO), 8.71 (d, 1H, Py-H, J = 8.5 Hz), 8.07 (d, 1H, Py-H, J = 2.6 Hz), 7.83 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.79 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.64 (d, 1H, Ar-H, J = 2.2 Hz), 6.94 (d, 1H, Ar-H, J = 8.5 Hz), 4.09 (t, 2H, OCH₂, J = 6.6 Hz), 4.07 (t, 2H, OCH₂, J = 6.6 Hz), 1.92-1.83 (m, 4H, 2 x CH₂), 1.48-1.39 (m, 8H, 4 x CH₂), 0.94 (t, 3H, CH₃, J = 7.0 Hz), 0.93 (t, 3H, CH₃, J = 7.0 Hz); ¹³C-NMR (CDCl₃): δC 192.1, 164.8, 155.4, 151.89, 150.8, 149.7, 145.0, 131.0, 125.7, 123.4, 120.9, 115.5, 112.8, 70.2, 70.0, 29.6, 29.5, 29.0, 23.3, 14.8; MS m/z (ESMS): 399 ([M]⁺, 20%), 277 ([M-OpyCO]⁺, 100%); IR ν/cm⁻¹ (nujol): 2924, 2854, 1728.

Following the same general procedure described for 19a, the following compounds were prepared:

3,4-Bisdiheptyloxybenzoic acid 6-formylpyridin-3-ester (19b): From compound 18 (0.50 g, 2.44 mmol), compound 12b (0.85 g, 2.44 mmol) and EDC (1.16 g, 60.55 mmol) in dry CH₂Cl₂ (50 mL) to yield a white solid (0.40 g, 40%); mp: 66-68 °C; ¹H-NMR (CDCl₃): δH 10.08 (s, 1H, CHO), 8.70 (d, 1H, Py-H, J = 2.6 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.82 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.79 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.64 (d, 1H, Ar-H, J = 2.2 Hz), 6.95 (d, 1H, Ar-H, J = 8.5 Hz), 4.09 (t, 2H, OCH₂, J = 6.6 Hz), 4.06 (t, 2H, OCH₂, J = 6.6 Hz), 1.89-1.83 (m, 4H, 2 x CH₂), 1.49-1.30 (m, 16H, 8 x CH₂), 0.89-0.84 (m, 6H, 2 x CH₃); ¹³C-NMR (CDCl₃): δC 192.2, 164.6, 152.7, 149.1, 148.1, 147.0,
3,4-Bisdinyloxybenzoic acid 6-formylpyridin-3-ester (19c): From compound 18 (0.50 g, 2.44 mmol), compound 12c (0.99 g, 2.44 mmol) and EDC (1.16 g, 60.55 mmol) in dry CH₂Cl₂ (50 mL). This yielded a white solid (0.45 g, 36%); mp: 68-70 °C; ¹H-NMR (CDCl₃): δH 10.08 (s, 1H, CHO), 8.71 (d, 1H, Py-H, J = 2.2 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.83 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.79 (dd, 1H, Py-H, J = 8.5, 2.2 Hz), 7.56 (d, 1H, Ar-H, J = 2.2 Hz), 6.94 (d, 1H, Ar-H, J = 8.5 Hz), 4.09 (t, 2H, OCH₂, J = 6.6 Hz), 1.89-1.82 (m, 4H, 2 x CH₂), 1.49-1.28 (m, 24H, 12 x CH₂), 0.89-0.85 (m, 6H, 2 x CH₃); ¹³C-NMR (CDCl₃): δC 192.1, 162.5, 153.7, 149.5, 148.5, 147.4, 142.7, 128.7, 123.4, 121.1, 118.6, 113.2, 110.5, 68.0, 67.7, 30.4, 28.1, 27.9, 27.8, 27.5, 24.5, 21.2, 12.6; MS m/z (ESMS): 534 ([M+Na]⁺, 85%); IR ν/cm⁻¹ (nujol): 2930, 2855, 1730.

3,4-Bisdidodecyloxybenzoic acid 6-formylpyridin-3-ester (19d): From compound 18 (0.50 mg, 2.44 mmol), compound 12d (1.20 g, 2.44 mmol) and EDC (1.16 g, 60.55 mmol) in dry CH₂Cl₂ (50 mL). This yielded a white solid (0.46 g, 32%); mp: 70-71 °C; ¹H-NMR (CDCl₃): δH 10.09 (s, 1H, CHO), 8.71 (d, 1H, Py-H, J = 2.6 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.83 (dd, 1H, Ar-H, J = 8.5, 2.2 Hz), 7.79 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.64 (d, 1H, Ar-H, J = 2.2 Hz), 6.95 (d, 1H, Ar-H, J = 8.5 Hz), 4.09 (t, 2H, OCH₂, J = 6.6 Hz), 4.07 (t, 2H, OCH₂, J = 6.6 Hz), 1.96-1.82 (m, 4H, 2 x CH₂), 1.49-1.26 (m, 36H, 18 x CH₂), 0.87 (t, 6H, 2 x CH₃, J = 6.6 Hz); ¹³C-NMR (CDCl₃): δC 192.1, 164.0, 154.5, 150.9, 149.9, 148.8, 144.2, 130.2, 124.8, 122.5, 120.0, 114.5, 111.9, 69.4, 69.1, 31.9, 29.6, 29.4, 29.1, 26.0, 22.7, 14.1; MS m/z (ESMS): 618 ([M+Na]⁺, 100%); IR ν/cm⁻¹ (nujol): 2929, 2856, 1731.

3,4,5-Trispentyloxybenzoic acid 6-formylpyridin-3-ester (20a): From compound 18 (0.50 g, 4.07 mmol), compound 13a (1.55 g, 4.07 mmol) and EDC (1.16 g, 6.06 mmol) in dry CH₂Cl₂ (50 mL). This yielded a brown oil (0.77 g, 40%); ¹H-NMR (CDCl₃): δH 10.09 (s, 1H, CHO), 8.70 (d, 1H, Py-H, J = 2.6 Hz), 8.08 (d, 1H, Py-H, J = 8.5 Hz), 7.77 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.39 (s, 2H, Ar-H), 4.07 (t, 2H, OCH₂, J = 6.6 Hz), 4.04 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 1.89-1.72 (m, 6H, 3 x CH₂), 1.50-1.26 (m, 12H, 6 x CH₂), 0.93 (t, 9H, 3 x CH₃, J = 7.0 Hz); ¹³C-NMR (CDCl₃): δC 192.2, 164.2, 153.3, 151.1, 150.3, 144.4, 144.0, 130.4, 122.8, 122.6, 109.0, 73.8, 69.6, 30.1, 29.1, 28.4, 22.6, 22.5, 14.1; MS m/z (EIMS): 485 ([M⁺, 15%], 363 ([M-OPyCHO]⁺, 100%), 293 ([M-OPyCHO-C₅H₁₀]⁺, 75%), 153 ([M-OPyCHO-(3xC₅H₁₀)]⁺, 30%); IR ν/cm⁻¹ (nujol): 2927, 2854, 1731.

3,4,5-Trisheptyloxybenzoic acid 6-formylpyridin-3-ester (20b): From compound 18 (0.50 g, 4.07 mmol), compound 13b (1.89 g, 4.07 mmol) and EDC (1.16 g, 6.06 mmol) in dry CH₂Cl₂ (50 mL). This yielded a brown oil (0.88 g, 39%); ¹H-NMR (CDCl₃): δH 10.09 (s, 1H, CHO), 8.70 (d, 1H, Py-H, J = 2.6 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.77 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.39 (s, 2H, Ar-H), 4.06 (t, 2H, OCH₂, J = 6.6 Hz), 4.06 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 1.88-1.72 (m, 6H, 3 x CH₂), 1.50-1.30 (m, 24H, 12 x CH₂), 0.88 (t, 9H, 3 x CH₃, J = 6.4 Hz); ¹³C-NMR (CDCl₃): δC 192.4, 164.4, 153.5, 151.3, 150.5, 144.5, 144.2, 130.6, 122.9, 122.8, 109.2, 74.0, 69.7, 32.3, 32.2, 29.6, 29.4, 26.4, 23.0, 14.4; MS m/z (ESMS): 592 ([M+Na]⁺, 100%); IR ν/cm⁻¹ (nujol): 2926, 2854, 1728.
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3,4,5-Bistrinonyloxybenzoic acid 6-formylpyridin-3-ester (20c): From compound 18 (0.50 g, 4.07 mmol), compound 13c (2.23 g, 4.07 mmol) and EDC (1.16 g, 60.55 mmol) in dry CH₂Cl₂ (50 mL). This yielded a white solid (0.89 g, 34%); mp: 34-37 °C; ¹H-NMR (CDCl₃): δH 10.08 (s, 1H, CHO), 8.69 (d, 1H, Py-H, J = 2.6 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.77 (dd, 1H, Py-H, J = 8.5, 2.6 Hz), 7.39 (s, 2H, Ar-H), 4.07 (t, 2H, OCH₂, J = 6.4 Hz), 4.04 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 1.87-1.71 (m, 6H, 3 x CH₃), 1.50-1.26 (m, 36H, 18 x CH₂), 0.87 (t, 3H, CH₃, J = 6.6 Hz), 0.86 (t, 6H, 2 x CH₃, J = 7.0 Hz); ¹³C-NMR (CDCl₃): δC 194.7, 166.7, 155.8, 153.6, 152.8, 146.8, 146.5, 132.9, 125.3, 125.1, 111.5, 76.3, 72.0, 34.5, 33.0, 32.3, 32.2, 32.0, 28.7, 25.3, 16.7; MS m/z (ESMS): 676 ([M+Na]⁺, 100%); IR μ/cm⁻¹ (nujol): 2927, 2855, 1730.

3,4,5-Trisdodecyloxybenzoic acid 6-formylpyridin-3-ester (20d): From compound 18 (0.50 g, 4.07 mmol), compound 13d (2.74 g, 2.44 mmol) and EDC (1.16 g, 60.55 mmol) in dry CH₂Cl₂ (50 mL). This yielded a white solid (0.89 g, 35%); mp: 41-43 °C; ¹H-NMR (CDCl₃): δH 10.08 (s, 1H, CHO), 8.69 (d, 1H, Py-H, J = 2.2 Hz), 8.07 (d, 1H, Py-H, J = 8.5 Hz), 7.77 (dd, 1H, Py-H, J = 8.5, 2.2 Hz), 7.39 (s, 2H, Ar-H), 4.06 (t, 2H, OCH₂, J = 6.6 Hz), 4.04 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 1.85-1.71 (m, 6H, 3 x CH₂), 1.49-1.25 (m, 54H, 27 x CH₂), 0.86 (t, 9H, 3 x CH₃, J = 6.6 Hz); ¹³C-NMR (CDCl₃): δC 191.3, 163.3, 152.4, 150.2, 149.4, 143.4, 143.1, 129.4, 121.8, 121.6, 108.1, 72.9, 68.6, 31.2, 29.6, 28.8, 28.6, 25.3, 21.9, 13.3; MS m/z (ESMS): 802 ([M+Na]⁺, 100%), 780 ([M+H]⁺, 20%); IR μ/cm⁻¹ (nujol): 2927, 2856, 1731.

6-{N-[4-{4-[(E)-[4-[(3,4-bis(pentyloxy)phenyl]carbonyloxy]pyridin-2-yl]methylidene}amino]phenyl)methyl}phenyl]carboximidoyl}pyridin-3-yl 3,4-bis(pentyloxy)benzoate (1a): To a solution of compound 19a (202 mg, 0.51 mmol) in anhydrous EtOH (4 mL) under N₂ atmosphere, 4,4’-methylene dianiline (50 mg, 0.25 mmol) was added. The reaction mixture was stirred and heated at 50 °C for 24 hrs under a N₂ atmosphere. The solid was collected through suction filtration and recrystallised in anhydrous PhMe. The yellow solid was collected through suction filtration (140 mg, 58%); mp: 158-159 °C; Calculated for C₅₉H₆₈N₄O₈: 73.72% C, 7.13% H, 5.83% N; found: 73.68% C, 7.10% H, 5.90% N; ¹H-NMR (CDCl₃): δH 8.63 (s, 2H, HC=N), 8.62 (d, 2H, Py-H, J = 2.2 Hz), 8.28 (d, 2H, Py-H, J = 8.5, 2.2 Hz), 7.83 (dd, 2H, Ar-H, J = 8.5, 1.8 Hz), 7.71 (dd, 2H, Py-H, J = 8.5, 2.2 Hz), 7.65 (d, 2H, Ar-H, J = 1.8 Hz), 7.26 (s, 8H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.5 Hz), 4.09 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 4.07 (t, 4H, 2 x OCH₂, J = 6.6 Hz), 4.05 (s, 2H, Ph₂CH₂), 1.90-1.81 (m, 8H, 4 x CH₂), 1.55-1.34 (m, 16H, 8 x CH₂), 0.94 (t, 6H, 2 x CH₃, J = 7.0 Hz), 0.93 (t, 6H, 2 x CH₃, J = 7.0 Hz); ¹³C-NMR (CDCl₃): δC 166.8, 161.5, 156.8, 154.4, 151.1, 151.4, 145.9, 142.3, 132.5, 132.3, 132.1, 127.2, 124.9, 123.9, 123.0, 117.1, 114.5, 71.9, 71.6, 43.5, 31.3, 31.2, 30.7, 24.5, 16.5; MS m/z (ESMS): 962 ([M+H]⁺, 100%); IR μ/cm⁻¹ (nujol): 2927, 2854, 1729, 1598.

Following the same general procedure described for the preparation of 1a, the following compounds were prepared:

6-{N-[4-{(4-[(E)-[4-(3,4-bis(heptyloxy)phenyl]carbonyloxy]pyridin-2-yl]methylidene}amino]phenyl)methyl}phenyl]carboximidoyl}pyridin-3-yl 3,4-bis(heptyloxy)benzoate (1b): From compound 19b (230 mg, 0.51 mmol), 4,4’-methylenedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (4 mL).
This yielded a pale yellow solid (186 mg, 69%); mp: 136-137 °C; Calculated for C_{67}H_{84}N_{4}O_{8}: 74.97% C, 7.89% H, 5.22% N; found: 74.88% C, 7.70% H, 5.18% N; 1H-NMR (CDCl_3): δ_H 8.63 (s, 2H, Py-H, J = 2.6 Hz), 8.28 (d, 2H, Py-H, J = 8.5 Hz), 7.83 (dd, 2H, Ar-H, J = 8.5, 2.1 Hz), 7.71 (dd, 2H, Py-H, J = 8.5, 2.6 Hz), 7.65 (d, 2H, Ar-H, J = 2.1 Hz), 7.26 (s, 8H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.5 Hz), 4.09 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.07 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.04 (s, 2H, Ph_2CH_2), 1.91-1.80 (m, 8H, 4 x CH_2), 1.55-1.34 (m, 32H, 16 x CH_2), 0.89 (t, 6H, 2 x CH_3, J = 6.99 Hz), 0.88 (t, 6H, 2 x CH_3, J = 6.99 Hz); 13C-NMR (CDCl_3): δ_C 165.5, 160.1, 155.5, 153.1, 150.1, 144.5, 140.9, 131.2, 130.9, 130.7, 125.8, 123.5, 122.5, 121.6, 115.8, 113.1, 70.5, 70.3, 42.2, 32.9, 30.3, 30.2, 27.1, 23.7, 15.2; MS m/z (ESMS): 1096 ([M+Na]^+), 100%; IR ν/cm⁻¹ (nujol): 2926, 2855, 1729, 1598.

6-{N-[4-{(E)-(5-{[3,4-bis(nonyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino}-phenyl}methylphenyl]carboximidoyl]pyridin-3-yl 3,4-bis(nonyloxy)benzoate (1c): From compound 19c (258 mg, 0.51 mmol), 4,4'-methylenedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (5 mL). This yielded a pale yellow solid (155 mg, 52%); mp: 129 °C; Calculated for C_{75}H_{100}N_{4}O_{8}: 75.98% C, 8.50% H, 4.73% N; found: 75.80% C, 8.40% H, 4.63% N; 1H-NMR (CDCl_3): δ_H 8.63 (s, 2H, HC=N), 8.62 (d, 2H, Py-H, J = 2.6 Hz), 8.29 (d, 2H, Py-H, J = 8.8 Hz), 7.83 (dd, 2H, Ar-H, J = 8.5, 1.8 Hz), 7.71 (dd, 2H, Py-H, J = 8.8, 2.6 Hz), 7.65 (d, 2H, Ar-H, J = 1.8 Hz), 7.26 (s, 8H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.5 Hz), 4.09 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.07 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.05 (s, 2H, Ph_2CH_2), 1.89-1.80 (m, 8H, 4 x CH_2), 1.49-1.29 (m, 48H, 24 x CH_2), 0.88 (t, 6H, 2 x CH_3, J = 6.99 Hz), 0.87 (t, 6H, 2 x CH_3, J = 6.99 Hz); 13C-NMR (CDCl_3): δ_C 166.0, 160.7, 156.0, 155.2, 153.6, 150.6, 150.5, 145.0, 141.4, 131.7, 131.4, 126.4, 124.0, 123.1, 122.1, 116.3, 113.6, 71.1, 70.8, 42.8, 33.5, 31.2, 31.0, 30.9, 30.8, 30.7, 27.6, 24.3, 15.7; MS m/z (ESMS): 1207 ([M+Na]^+); IR ν/cm⁻¹ (nujol): 2926, 2854, 1727, 1598.

6-{N-[4-{(E)-(5-{[3,4-bis(dodecyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino}-phenyl]methylphenyl]carboximidoyl]pyridin-3-yl 3,4-bis(dodecyloxy)benzoate (1d): From compound 19d (301 mg, 0.51 mmol), 4,4'-methylenedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (6 mL). This yielded a pale yellow solid (190 mg, 56%); mp: 126 °C; Calculated for C_{87}H_{124}N_{4}O_{8}: 77.18% C, 9.23% H, 4.14% N; found: 77.23% C, 9.31% H, 4.17% N; 1H-NMR (CDCl_3): δ_H 8.63 (s, 2H, HC=N), 8.62 (d, 2H, Py-H, J = 2.6 Hz), 8.29 (d, 2H, Py-H, J = 8.8 Hz), 7.83 (dd, 2H, Ar-H, J = 8.5, 1.8 Hz), 7.71 (dd, 2H, Py-H, J = 8.8, 2.6 Hz), 7.65 (d, 2H, Ar-H, J = 1.8 Hz), 7.26 (s, 8H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.5 Hz), 4.09 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.07 (t, 4H, 2 x OCH_2, J = 6.6 Hz), 4.05 (s, 2H, Ph_2CH_2), 1.89-1.80 (m, 8H, 4 x CH_2), 1.49-1.29 (m, 48H, 24 x CH_2), 0.88 (t, 6H, 2 x CH_3, J = 7.0 Hz), 0.87 (t, 6H, 2 x CH_3, J = 7.0 Hz); 13C-NMR (CDCl_3): δ_C 165.5, 160.2, 155.6, 154.7, 153.1, 150.2, 150.1, 144.2, 141.0, 131.3, 131.1, 126.4, 123.6, 122.7, 121.7, 115.7, 110.0, 71.1, 70.8, 42.8, 33.5, 31.2, 31.0, 30.9, 30.8, 30.7, 27.6, 24.3, 15.7; MS m/z (ESMS): 1354 ([M]^+); IR ν/cm⁻¹ (nujol): 2926, 2854, 1727, 1598.

6-{N-[4-{(E)-(5-{[3,4,5-tris(pentyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino}-phenyl]methylphenyl]carboximidoyl]pyridin-3-yl 3,4,5-tris(pentyloxy)benzoate (2a): From compound 20a (245 mg, 0.51 mmol), 4,4'-methylenedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (4 mL). This yielded a yellow solid (151 mg, 53%). mp: 67 °C; Calculated for C_{69}H_{88}N_{4}O_{10}: 73.12% C, 7.83%
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H, 4.94% N; found: 73.16% C, 7.87% H, 4.89% N; \( ^1H-NMR (CDCl_3): \delta_H 8.63\) (s, 2H, HC=N), 8.61 (d, 2H, Py-H, \( J = 2.6\) Hz), 8.29 (d, 2H, Py-H, \( J = 8.8\) Hz), 7.71 (dd, 2H, Py-H, \( J = 8.8, 2.6\) Hz), 7.41 (s, 4H, Ar-H), 7.26 (s, 8H, Ar-H), 4.07 (t, 4H, \( 2 \times OCH_2, J = 6.6\) Hz), 4.05 (t, 8H, \( 4 \times OCH_2, J = 6.6\) Hz), 4.05 (s, 2H, Ph\( 2CH_2\)), 1.89-1.72 (m, 12H, \( 6 \times CH_2\)), 1.53-1.31 (m, 24H, \( 12 \times CH_2\)), 0.93 (t, 18H, \( 6 \times CH_3, J = 7.0\) Hz); \( ^13C-NMR (CDCl_3): \delta_C 164.7, 159.3, 153.4, 152.4, 149.3, 149.1, 143.9, 143.7, 140.2, 130.4, 130.2, 123.2, 122.7, 121.8, 109.1, 74.0, 69.7, 41.5, 31.3, 29.3, 28.6, 22.9, 22.8, 14.4; MS m/z (ESMS): 1133 ([M^+]\(^+\)); IR \( \nu/cm\(^{-1}\) (nujol): 2930, 2857.

6-\{N-\{4-\{(E)-(\{5-\{3,4,5-tris(heptyloxy)phenyl\}carbonyloxy\}pyridin-2-yl\}methylidene\}amino\}phenyl\}methyl\}phenyl\}carboximidoyl\}pyridin-3-yl 3,4,5-tris(heptyloxy)benzoate (2b): From compound 20b (287 mg, 0.51 mmol), 4,4'-methyleneedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (4 mL). This yielded a yellow solid (197 mg, 60%); mp: 54-56 °C; Calculated for C\(_{81}\)H\(_{112}\)N\(_4\)O\(_{10}\): 74.73% C, 8.67% H, 4.30% N; found: 74.78% C, 8.70% H, 4.32% N; \( ^1H-NMR (CDCl_3): \delta_H 8.63\) (s, 2H, HC=N), 8.61 (d, 2H, Py-H, \( J = 2.6\) Hz), 8.29 (d, 2H, Py-H, \( J = 8.5\) Hz), 7.70 (dd, 2H, Py-H, \( J = 8.5, 2.6\) Hz), 7.40 (s, 4H, Ar-H), 7.26 (s, 8H, Ar-H), 4.07 (t, 4H, \( 2 \times OCH_2, J = 6.4\) Hz), 4.05 (t, 8H, \( 4 \times OCH_2, J = 6.3\) Hz), 4.05 (s, 2H, Ph\( 2CH_2\)), 1.88-1.71 (m, 12H, \( 6 \times CH_2\)), 1.50-1.27 (m, 48H, \( 12 \times CH_2\)), 0.88 (t, 6H, \( 2 \times CH_3, J = 7.0\) Hz), 0.87 (t, 12H, \( 4 \times CH_3, J = 7.0\) Hz); \( ^13C-NMR (CDCl_3): \delta_C 163.1, 157.7, 151.9, 150.1, 147.7, 147.6, 142.4, 142.2, 138.6, 128.8, 128.6, 121.6, 121.2, 120.2, 107.6, 72.4, 68.2, 39.9, 30.7, 30.6, 29.1, 28.1, 28.0, 27.8, 24.8, 21.4, 12.9; MS m/z (ESMS): 1302 ([M+H]^+); IR \( \nu/cm\(^{-1}\) (nujol): 2930, 2857, 1744s, 1590.

6-\{N-\{4-\{(E)-(\{5-\{3,4,5-tris(nonyloxy)phenyl\}carbonyloxy\}pyridin-2-yl\}methylidene\}amino\}phenyl\}methyl\}phenyl\}carboximidoyl\}pyridin-3-yl 3,4,5-tris(nonyloxy)benzoate (2c): From compound 20c (330 mg, 0.51 mmol), 4,4'-methyleneedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (5 mL). This yielded a yellow solid (241 mg, 65%); mp: 54-56 °C; Calculated for C\(_{93}\)H\(_{136}\)N\(_4\)O\(_{10}\): 75.98% C, 9.32% H, 3.81% N; found: 75.90% C, 9.27% H, 3.85% N; \( ^1H-NMR (CDCl_3): \delta_H 8.63\) (s, 2H, HC=N), 8.61 (d, 2H, Py-H, \( J = 2.6\) Hz), 8.29 (d, 2H, Py-H, \( J = 8.5\) Hz), 7.70 (dd, 2H, Py-H, \( J = 8.5, 2.6\) Hz), 7.40 (s, 4H, Ar-H), 7.26 (s, 8H, Ar-H), 4.07 (t, 4H, \( 2 \times OCH_2, J = 6.6\) Hz), 4.05 (t, 8H, \( 4 \times OCH_2, J = 6.6\) Hz), 4.05 (s, 2H, CH\(_2\)), 1.88-1.71 (m, 12H, \( 6 \times CH_2\)), 1.50-1.21 (m, 72H, \( 36 \times CH_2\)), 0.88 (t, 6H, \( 2 \times CH_3, J = 7.0\) Hz), 0.87 (t, 12H, \( 4 \times CH_3, J = 7.0\) Hz); \( ^13C-NMR (CDCl_3): \delta_C 164.4, 159.0, 153.1, 152.1, 149.0, 148.8, 143.6, 143.4, 139.9, 130.1, 129.8, 122.8, 122.4, 121.4, 108.8, 73.7, 69.4, 41.4, 31.9, 30.4, 29.7, 29.6, 29.4, 29.3, 26.1, 22.7, 14.1; MS m/z (ESMS): 1471 ([M+H]^+); IR \( \nu/cm\(^{-1}\) (nujol): 2930, 2857, 1744s, 1590.

6-\{N-\{4-\{(E)-(\{5-\{3,4,5-tris(dodecyloxy)phenyl\}carbonyloxy\}pyridin-2-yl\}methylidene\}amino\}phenyl\}methyl\}phenyl\}carboximidoyl\}pyridin-3-yl 3,4,5-tris(dodecyloxy)benzoate (2d): From compound 20d (398 mg, 0.51 mmol), 4,4'-methyleneedianiline (50 mg, 0.25 mmol) and anhydrous EtOH (6 mL). This yielded a yellow solid (291 mg, 67%); mp 51 °C; Calculated for C\(_{111}\)H\(_{172}\)N\(_4\)O\(_{10}\): 77.40% C, 10.06% H, 3.25% N; found: 77.33% C, 10.01% H, 3.27% N; \( ^1H-NMR (CDCl_3): \delta_H 8.63\) (s, 2H, HC=N), 8.61 (d, 2H, Py-H, \( J = 2.6\) Hz), 8.29 (d, 2H, Py-H, \( J = 8.8\) Hz), 7.70 (dd, 2H, Py-H, \( J = 8.8, 2.6\) Hz), 7.40 (s, 4H, Ar-H), 7.27 (s, 8H, Ar-H), 4.06 (t, 4H, \( 2 \times OCH_2, J = 6.4\) Hz), 4.04 (t, 8H, \( 4 \times OCH_2, J = 6.3\) Hz), 4.04 (s, 2H, Ph\( 2CH_2\)), 1.89-1.71 (m, 12H, \( 6 \times CH_2\)), 1.48-1.25 (m, 108H, 54 x
6-{N-[3-((E)-[5-([3,4-bis(pentyloxy)phenyl]carbonyloxy)pyridin-2-yl]methylidene)amino]phenyl}methyl}phenyl]carboximidoyl]pyridin-3-yl 3,4-bis(pentyloxy)benzoate (3a): From compound 19a (60 mg, 0.16 mmol), 3,3'-methylenedianiline (10 mg, 0.08 mmol) and anhydrous EtOH (2 mL). This yielded a brown oil (60 mg, 85%). 1H-NMR (CDCl3): δH 8.61 (s, 2H, HC=N), 8.60 (d, 2H, Py-H, J = 2.3 Hz), 8.27 (d, 2H, Py-H, J = 8.7 Hz), 7.82 (dd, 2H, Ar-H, J = 8.5, 2.1 Hz), 7.71 (dd, 2H, Py-H, J = 8.7, 2.1 Hz), 7.61 (d, 2H, Ar-H, J = 2.1 Hz), 7.35 (t, 2H, Ar-H, J = 8.5 Hz), 7.15 (m, 6H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.5 Hz), 4.07 (m, 10H, Ph2CH2, OCH2), 1.88-1.68 (m, 8H, 4 x CH2), 1.52-1.31 (m, 16H, 8 x CH2), 0.93 (t, 12H, 4 x CH3, J = 7.0 Hz); 13C-NMR (CDCl3): δC 160.0, 152.2, 151.5, 149.3, 143.8, 130.6, 130.5, 128.8, 127.9, 125.1, 122.8, 122.4, 120.9, 119.2, 115.0, 112.3, 42.2, 29.2, 29.1, 28.6, 22.9, 14.4; MS m/z (+ve FAB): 961 ([M]+, 80%).

6-{N-[3-((E)-[5-([3,4-bis(heptyloxy)phenyl]carbonyloxy)pyridin-2-yl]methylidene)amino]phenyl}methyl}phenyl]carboximidoyl]pyridin-3-yl 3,4-bis(heptyloxy)benzoate (3b): From compound 19b (50 mg, 0.11 mmol), 3,3'-methylenedianiline (10 mg, 0.06 mmol) and anhydrous EtOH (2 mL). This yielded a brown oil (40 mg, 76%). 1H-NMR (CDCl3): δH 8.61 (s, 2H, HC=N), 8.61 (d, 2H, Py-H, J = 2.5 Hz), 8.27 (d, 2H, Py-H, J = 8.6 Hz), 7.83 (dd, 2H, Ar-H, J = 8.3, 2.0 Hz), 7.71 (dd, 2H, Py-H, J = 8.6, 2.3 Hz), 7.65 (d, 2H, Ar-H, J = 2.0 Hz), 7.35 (t, 2H, Ar-H, J = 7.5 Hz), 7.16-7.13 (m, 6H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.3 Hz), 4.09-4.05 (m, 10H, Ph2CH2, 4 x OCH2), 1.88-1.71 (m, 8H, 4 x CH2), 1.52-1.30 (m, 32H, 16 x CH2), 0.93 (m, 12H, 4 x CH3); 13C-NMR (CDCl3): δC 160.0, 143.8, 130.5, 129.8, 127.8, 125.1, 122.8, 122.4, 119.1, 115.0, 112.4, 32.2, 29.6, 29.4, 26.4, 26.3, 23.0, 14.5; MS m/z (+ve FAB): 1073 ([M]+); IR ν/cm⁻¹ (nujol): 2911, 2851, 1729, 1593, 1516.

6-{N-[3-((E)-[5-([3,4-bis(dodecyloxy)phenyl]carbonyloxy)pyridin-2-yl]methylidene)amino]phenyl}methyl}phenyl]carboximidoyl]pyridin-3-yl 3,4-bis(dodecyloxy)benzoate (3c): From compound 19d (70 mg, 0.12 mmol), 3,3'-methylenedianiline (10 mg, 0.06 mmol) and anhydrous EtOH (2 mL). This yielded a white solid (70 mg, 83%); Calculated for C87H124N4O8 • H2O: 76.2% C, 9.1% H, 4.1% N; found: 75.9% C, 9.0% H, 3.9% N; 1H-NMR (CDCl3): δH 8.60 (s, 2H, HC=N), 8.60 (d, 2H, Py-H, J = 2.5 Hz), 8.27 (d, 2H, Py-H, J = 8.6 Hz), 7.83 (dd, 2H, Ar-H, J = 8.3, 2.0 Hz), 7.71 (dd, 2H, Py-H, J = 8.6, 2.3 Hz), 7.65 (d, 2H, Ar-H, J = 2.0 Hz), 7.35 (t, 2H, Ar-H, J = 7.5 Hz), 7.16-7.13 (m, 6H, Ar-H), 6.94 (d, 2H, Ar-H, J = 8.3 Hz), 4.09-4.05 (m, 10H, Ph2CH2, 4 x OCH2), 1.88-1.71 (m, 8H, 4 x CH2), 1.52-1.30 (m, 32H, 16 x CH2), 0.93 (m, 12H, 4 x CH3); 13C-NMR (CDCl3): δC 160.0, 143.8, 130.5, 129.8, 127.8, 125.1, 122.8, 122.4, 119.1, 115.0, 112.4, 32.2, 29.6, 29.4, 26.4, 26.3, 23.0, 14.5; MS m/z (+ve FAB): 1354 ([M]+); IR ν/cm⁻¹ (nujol): 2933, 2840, 1734, 1685, 1593, 1516.

6-{N-[3-((E)-[5-([3,4,5-tris(pentyloxy)phenyl]carbonyloxy)pyridin-2-yl]methylidene)amino]phenyl}methyl}phenyl]carboximidoyl]pyridin-3-yl 3,4,5-tris(pentyloxy)benzoate (4a): From compound 20a (79 mg, 0.16 mmol), 3,3'-methylenedianiline (16 mg, 0.08 mmol) and anhydrous EtOH (2 mL). This yielded a brown oil (52 mg, 56%); Calculated for C69H88N4O10 73.12% C, 7.83% H, 4.94% N; found: 73.16% C, 7.87% H, 4.89% N; 1H-NMR (CDCl3): δH 8.60 (s, 2H, HC=N), 8.60 (d, 2H, Py-H, J = 2.3 Hz), 8.07 (t, 18H, 9 x CH2, J = 6.6 Hz); 13C-NMR (CDCl3): δC 162.5, 157.1, 151.2, 150.2, 147.1, 146.9, 141.7, 141.5, 138.0, 128.2, 128.0, 120.9, 120.5, 119.6, 106.9, 71.8, 67.5, 30.1, 28.5, 27.8, 27.5, 24.2, 20.8, 12.3; MS m/z (ESMS): 1744 ([M+Na]+); IR ν/cm⁻¹ (nujol): 2930, 2857, 1729, 1598.
6-{N-[3-{[(E)-[(5-{[3,4,5-tris(heptyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino]-phenyl}methyl]phenyl}carboximidoyl]pyridin-3-yl 3,4,5-tris(heptyloxy)benzoate (4b): From compound 20b (287 mg, 0.51 mmol), 3,3'-methylene dianiline (50 mg, 0.25 mmol) and anhydrous EtOH (4 mL). This yielded a brown oil (195 mg, 59%); Calculated for C81H112N4O10 74.73% C, 8.67% H, 4.30% N; found: 74.78% C, 8.70% H, 4.32% N; 1H-NMR (CDCl3): δH 8.60 (s, 2H, HC=N), 8.60 (d, 2H, Py-H, J = 2.6 Hz), 8.28 (d, 2H, Py-H, J = 8.6 Hz), 7.70 (dd, 2H, Py-H, J = 8.6, 2.6 Hz), 7.40 (s, 4H, Ar-H), 7.35 (t, 2H, Ar-H, J = 7.7 Hz), 7.16-7.13 (m, 6H, Ar-H), 4.07 (s, 2H, Ph2CH2), 4.07 (t, 4H, 2 x OCH2, J = 6.6 Hz), 4.04 (t, 8H, 4 x OCH2, J = 6.6 Hz), 1.88-1.71 (m, 12H, 6 x CH2), 1.52-1.30 (m, 48H, 24 x CH2), 0.88 (t, 18H, 6 x CH3, J = 7.0 Hz); 13C-NMR (CDCl3): δC 164.8, 159.9, 153.5, 152.4, 151.5, 149.2, 144.0, 143.8, 142.8, 129.8, 127.9, 123.2, 122.8, 122.4, 119.1, 109.2, 74.0, 69.8, 42.2, 32.3, 32.2, 30.8, 29.7, 29.6, 29.4, 26.4, 23.0, 14.5; MS m/z (ESMS): 1324 ([M+Na]+), 1303; IR ν/cm−1 (nujol): 2927, 2854, 1739, 1586.

6-{N-[3-{[(E)-[(5-{[3,4,5-tris(nonyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino]-phenyl}methyl]phenyl}carboximidoyl]pyridin-3-yl 3,4,5-tris(nonyloxy)benzoate (4c): From compound 20c (160 mg, 0.25 mmol), 3,3'-methylenedianiline (24 mg, 0.12 mmol) and anhydrous EtOH (4 mL). This yielded a white solid (117 mg, 65%); mp: 51°C; Calculated for C93H136N4O10 75.98% C, 9.32% H, 3.81% N; found: 75.90% C, 9.37% H, 3.85% N; 1H-NMR (CDCl3): δH 8.60 (s, 2H, CHN), 8.60 (d, 2H, Py-H, J = 2.2 Hz), 8.28 (d, 2H, Py-H, J = 8.6 Hz), 7.69 (dd, 2H, Py-H, J = 8.6, 2.2 Hz), 7.40 (s, 4H, Ar-H), 7.35 (t, 2H, Ar-H, J = 7.7 Hz), 7.16-7.14 (m, 6H, Ar-H), 4.06 (s, 2H, Ph2CH2), 4.06 (t, 4H, 2 x OCH2, J = 6.6 Hz), 4.04 (t, 8H, 4 x OCH2, J = 6.6 Hz), 1.87-1.71 (m, 12H, 6 x CH2), 1.48-1.27 (m, 72H, 36 x CH2), 0.88 (t, 6H, 2 x CH3, J = 7.0 Hz), 0.87 (t, 12H, 4 x CH3, J = 7.0 Hz); 13C-NMR (CDCl3): δC 163.6, 158.7, 152.3, 151.2, 150.3, 148.0, 142.8, 142.6, 141.3, 129.3, 128.6, 126.7, 122.0, 121.6, 121.2, 118.0, 108.0, 72.8, 68.6, 41.0, 31.1, 29.6, 28.9, 28.8, 28.6, 28.5, 25.3, 21.9, 13.3; MS m/z (ESMS): 1471 ([M+H]+); IR ν/cm−1 (nujol): 2927, 2854, 1739, 1586.

6-{N-[3-{[(E)-[(5-{[3,4,5-tris(dodecyloxy)phenyl]carbonyloxy}pyridin-2-yl)methylidene]amino]-phenyl}methyl]phenyl}carboximidoyl]pyridin-3-yl 3,4,5-tris(dodecyloxy)benzoate (4d): From compound 20d (150 mg, 0.19 mmol), 3,3'-methylenedianiline (19 mg, 0.10 mmol) and anhydrous EtOH (4 mL). This yielded a white solid (110 mg, 67%); mp: 55°C; Calculated for C111H172N4O10 77.40% C, 10.06% H, 3.25% N; found: 77.33% C, 10.01% H, 3.27% N; 1H-NMR (CDCl3): δH 8.60 (s, 2H, CHN), 8.60 (d, 2H, Py-H, J = 2.6 Hz), 8.29 (d, 2H, Py-H, J = 8.5 Hz), 7.69 (dd, 2H, Py-H, J = 8.5, 2.6 Hz), 7.40 (s, 4H, Ar-H), 7.35 (t, 2H, Ar-H, J = 7.7 Hz), 7.16-7.14 (m, 6H, Ar-H), 4.06 (s, 2H, Ph2CH2), 4.06 (t, 4H, 2 x OCH2, J = 6.6 Hz), 4.07 (t, 8H, 4 x OCH2, J = 6.6 Hz), 1.87-1.71 (m, 12H, 6
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x CH₂), 1.48-1.25 (m, 108H, 54 x CH₂), 0.87 (t, 18H, 6 x CH₃, J = 6.6 Hz); ¹³C-NMR (CDCl₃): δC 164.3, 159.4, 153.0, 151.9, 151.0, 148.7, 143.5, 143.3, 142.0, 130.0, 129.3, 127.4, 122.7, 122.3, 122.0, 118.7, 108.7, 73.6, 69.3, 41.7, 31.9, 30.3, 29.6, 29.3, 26.0, 22.6, 14.0; MS m/z (ESMS): 1744 ([M+Na]⁺); IR ν/cm⁻¹ (nujol): 2927, 2854, 1735, 1585.

[Cu₂(3a)₂][PF₆]₂: To a solution of compound 3a (25 mg, 0.026 mmol) in propan-2-ol (5 mL) under a nitrogen atmosphere, [Cu(MeCN)₄][PF₆] (10 mg, 0.026 mmol) was added to give a dark red solution, which was heated under reflux overnight and then cooled to room temperature. A dark red solid precipitated from the solution on standing and was collected by filtration and washed with diethyl ether (41 mg, 67 %); Calculated for Cu₂C₁₁₈H₁₃₆N₈O₁₆P₂F₁₂·H₂O: 59.7% C, 5.9% H, 4.7% N; found: 59.4% C, 5.9%, 5.0% N; ¹H-NMR (CD₂Cl₂): δH 9.04 (br, 4H, HC=N), 8.46 (br, 4H, Py-H), 8.25 (br, 4H, Py-H), 8.08 (d, 4H, Ar-H, J = 8.0 Hz), 7.79 (d, 4H, Py-H, J = 8.6 Hz), 7.60 (s, 4H, Ar-H), 7.27 (t br, 4 H, Ar-H, J = 8.6 Hz), 7.00 (s br, 12H, Ar-H), 6.96 (d, 4H, Ar-H, J = 8.5 Hz), 4.09 (t, 8H, 4 x OCH₂, J = 6.5 Hz), 4.04 (t, 8H, 4 x OCH₂, J = 6.5 Hz), 3.69 (br s, 4H, Ph₂CH₂), 1.88-1.68 (m, 16H, 8 x CH₂), 1.52-1.31 (m, 32H, 16 x CH₂), 0.96 (q, 24H, 12 x CH₃, J = 7.0 Hz); m/z (+ve FAB MS): 2194 [([Cu₂(3a)₂][PF₆]⁺); MS m/z (ESMS): 1024 [([Cu 2(3a)₂]²⁺); IR ν/cm⁻¹ (solid): 2953, 2926, 2867, 1727, 1594, 1556, 1521; UV/Vis (CH₂Cl₂) λ max (ε, L mol⁻¹ cm⁻¹): 495 (9,500), 312 (83,600) nm.

[Cu₂(3b)₂][PF₆]₂: The same procedure as described for the preparation of compound [Cu₂(3a)₂][PF₆]₂ was followed, using compound 3b (12 mg, 0.011 mmol) and [Cu(MeCN)₄][PF₆] (4 mg, 0.011 mmol). This yielded a dark red solid (20 mg, 70 %); ¹H-NMR (CD₂Cl₂): δH 9.03 (br s, 4H, HC=N), 8.53 (br s, 4H, Py-H), 8.23 (d, 4H, Py-H, J = 8.3 Hz), 8.08 (d, J = 4H, Ar-H, 8.3 Hz), 7.77 (d, 4H, Py-H, J = 8.5 Hz), 7.59 (s, 4H, Ar-H), 7.25 (br t, 4H, J = 7.5 Hz), 7.00 (s br, 12H, Ar-H), 6.98 (br s, 4H, Ar-H), 4.08 (t, 8H, 4 x OCH₂, J = 6.5 Hz), 4.02 (t, 8H, 4 x OCH₂, J = 6.5 Hz), 3.66 (br s, 4H, Ph₂CH₂), 1.88-1.71 (m, 16H, 4 x CH₂), 1.52-1.30 (m, 64H, 32 x CH₂), 0.90 (m, 24H, 12 x CH₃); m/z (+ve FAB MS): 2419 [([Cu₂(3b)₂][PF₆]⁺); MS m/z (ESI MS): [Cu 2(3b)₂]²⁺; IR ν/cm⁻¹ (solid): 2922, 2852, 1727, 1595, 1556, 1513; UV/Vis (CH₂Cl₂) λ max (ε, L mol⁻¹ cm⁻¹): 480 (11,400), 294 (94,600) nm.

[Cu₂(3c)₂][PF₆]₂: The same procedure as described for the preparation of compound [Cu₂(3a)₂][PF₆]₂ was followed, using compound 3c (24 mg, 0.018 mmol) and [Cu(MeCN)₄][PF₆] (7 mg, 0.018 mmol). This yielded a dark red solid (56 mg, 65 %); The ¹H-NMR spectrum of the red material was very broad and the sample did not ionise well in ESI-MS; IR ν/cm⁻¹ (solid): 2919, 2853, 1732, 1662, 1600, 1508; UV/Vis (CH₂Cl₂) λ max (ε, L mol⁻¹ cm⁻¹): 482 (7 400), 298 (94 700) nm.

4. Conclusions

In summary, we have successfully synthesised a series of novel banana-shaped compounds, in which the bend unit is formed by a 4,4'-methylenedianiline or 3,3'-methylenedianiline core bearing two symmetric pyridylimine linkages. Also, a number of complexes [Cu₂(3a-c)₂][PF₆]₂ were formed by coordination with Cu(I) cations. Mass spectrometry techniques have shown that dinuclear double stranded arrays were formed. Thermal analyses of the ligands 1a-d, 2a-d, 3a-c and 4a-d and the metal...
complexes $[\text{Cu}_2(3\text{a-c})_2][\text{PF}_6]_2$ revealed that these do not display any mesophase behavior. However, the generic structure of the target series 1a-d, 2a-d, 3a-c and 4a-d appears to fulfill, in principle, the same criteria of the banana-shaped mesogens known to date [37]. Further work is being carried out to prepare and investigate the liquid crystalline properties of the Cu (I) complexes formed from ligands 1a-d, 2a-d and 4a-d, because such metal containing structures conjure up potential application of magnetic LC phases.

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References and Notes

1. Niori, T.; Sekine, T.; Watanabe, J.; Frukawa, T.; Takezoe, H. Distinct Ferroelectric Smectic Liquid Crystals Consisting of Achiral Molecules with Banana Shape. *Mol. Cryst. Liq. Cryst.* 1997, 301, 337-342.
2. Sekine, T.; Takanishi, Y.; Niori, T.; Watanabe, J.; Takezoe, T. Spontaneous Helix Formation in Smectic Liquid Crystals Comprising Achiral Molecules. *J. Mater. Chem.* 1997, 7, 1307-1309.
3. Matsumaga, Y.; Miyamoto, S. Mesomorphic Behavior of 2,4-Bis-(4-alkoxybenzylidene) Cyclopentanones and Related Compounds. *Mol. Cryst. Liq. Cryst.* 1993, 237, 311-317.
4. Cai, R.; Samulski, E. New Thermotropic Liquid Crystals Derived from Thiophene. *Liq. Cryst.*, 1991, 9, 617-634.
5. Niori, T.; Sekine, T.; Watanabe, T.; Furukawa, J.; Takezoe, H. Distinct Ferroelectric Smectic Liquid Crystals Consisting of Banana Shaped Achiral Molecules. *J. Mater. Chem.* 1996, 6, 1231-1233.
6. Weissflog, W.; Lischka, C.H.; Kruth, H. Proceeding of the European Conference on Liquid Crystals, Science and Technology, Zakopane, Poland, December 10-11, 1997, Volume 3-8, pp. 126-132.
7. Pelzl, G.; Diele, S.; Weissflog, W. Banana-Shaped Compounds – A New Field of Liquid Crystals. *Adv. Mater.* 1999, 11, 707-724.
8. Vill, V. *Landolt-Bornstein: Numerical data and functional relationship in science and technology, New Series;* Heidelberg: Berlin, Germany, 1992-1997.
9. Galyametdino, Y.G.; Ovchinnikor, I.V. Complexes of Liquid Crystal O-hydroxyazo Compounds with Cu$^{2+}$ and Pd$^{2+}$ Ions. *Russ. Chem. Bull.* 1991, 40, 2505-2508.
10. Hudson, S.A.; Maitlis, P.M. Metallogens. Synthesis, Properties and Applications. *Chem. Rev.* 1993, 93, 861-873.
11. Turanov, A.N.; Ovchinnikor, I.V.; Galyametdino, Y.G.; Ivanova, G.I.; Goncharo, V.A. Magnetic Anisotropy of Liquid Crystals Based on Lanthanide Mesogenic Complexes. *Russ. Chem. Bull.* 1999, 48, 690-693.
12. Bruce, D.W.; Liu, X.-H. Liquid Crystalline Complexes of Octahedral Manganese (I). *Chem. Commun.* 1994, 729-730.
13. Rowe, K.E; Bruce, D.W. The Synthesis and Mesomorphism of Di-, Tetra- and Hexa-Catenar Liquid Crystals Based on 2, 2'-Bipyridine. *J. Mater. Chem.* **1998**, *8*, 331-341.
14. Liu, X.-H.; Henrich, B.; Manners, I.; Guillon, D., Bruce, D.W. The Synthesis, Mesomorphism and Mesophase Structure of Anisotropic Imines and their Complexes with Rhenium (I). *J. Mater. Chem.* **2000**, *10*, 637-644.
15. Fazio, D.; Mongin. C.; Donnio, B.; Galerne, Y.; Guillon, D., Bruce, D.W. Bending and Shaping: Cubics, Calamities and Columns. *J. Mater. Chem.* **2001**, *11*, 2852-2863.
16. Donnio, B.; Bruce, D.W. Metallomesogens. In *Structure and Bonding*, Mingos, D.M.P., Ed.; Springer-Verlag: Heidelberg, Berlin, Germany, 1999; Volume 95, Chapter 5, p. 193.
17. El-ghayoury, A.; Douce, L.; Skoulios, A.; Ziesessel, R. Cation-Induced Macroscopic Ordering of Non-Mesomorphic Modules—A New Application for Metallohelicates. *Angew. Chem. Int. Ed.* **1998**, *37*, 2205-2208.
18. Hannon, M.J.; Painting, C.L.; Jackson, A.; Hamblin, J.; Errington, W. An Inexpensive Approach to Supramolecular Architecture. *Chem. Commun.* **1997**, 1807-1808.
19. Childs, L.J.; Hannon, M.J. Helices and Helicates, *Supramolecular Chem.* **2004**, *16*, 7-12.
20. Childs, L.J., Alcock, N.W., Hannon, M.J., Assembly of Nano-Scale Circular Supramolecular Arrays through $\pi-\pi$ aggregation of Arc-Shaped Helicate Units. *Angew. Chem. Intl. Ed.* **2001**, *40*, 1079-1081.
21. Childs, L.J., Pascu, M., Clarke, A.J., Alcock, N.W., Hannon, M.J. Using Non-Covalent Intra-Strand and Inter Strand Interactions to Prescribe Helix Formation within a Metallosupramolecular System. *Chem. Eur. J.* **2004**, *10*, 4291-4300.
22. Pelzl, G.; Diele, S.; Jakli, A.; Lischka, C.H.; Wirth, I.; Weissflog, W. Helical Superstructures in a Novel Smectic Mesophase Formed by Achiral Banana-Shaped Molecules. *Liq. Cryst.* **1999**, *26*, 135-139.
23. Shen, D.; Diele, S.; Pelzl, G.; Wirth, I.; Tschierske, C. Designing Banana-Shaped Liquid Crystals without Schiff's Base Units: m-Terphenyls, 2,6-Diphenylpyridines and V-Shaped Tolane Derivatives. *J. Mater. Chem.* **1991**, *9*, 661-672.
24. Shen, D.; Tschierske, C.; Diele, S.; Wirth, I. A Novel Class of Non-Chiral Banana-Shaped Liquid Crystals with Ferroelectric Properties. *Chem. Commun.* **1998**, 2573-2574.
25. Pelzl, G.; Diele, S.; Grande, S.; Jakli, A.; Lischka, C.H.; Kresse, H.; Schmalfuss, H.; Wirth, I.; Weissflog, W. Structural and Electro-Optical Investigations of the Smectic Phase of Chlorine-Substituted Banana-Shaped Compounds. *Liq. Cryst.* **1999**, *26*, 401-413.
26. Levitsky, I.A.; Kishikawa, K.; Eichhorn, S.H; Swagger, T.M. Exciton Coupling and Dipolar Correlations in a Columnar Liquid Crystal: Photophysics of a Bent-Rod Hexacatenar Mesogen. *J. Am. Chem. Soc.* **2000**, *122*, 2474-2479.
27. Weissflog, W.; Lischka, C.; Benne, I.; Scharf, T.; Pelzl, G.; Diele, S.; Kruth, H. *Proc. SPIE: Int. Soc. Opt. Eng.* **1998**, *14*, 3319-3321.
28. Dingemans, T.J.; Samulski, E.T. Non-Linear Boomerang-Shaped Liquid Crystals Derived from 2,5-Bis(p-hydroxyphenyl)-1,3,4-Oxadiazole. *Liq. Cryst.* **2000**, *27*, 131-136.
29. Matraszek, J.; Mieczkowski, J.; Szydlowska, J.; Gorecka, E. Nematic Phase Formed by Banana-Shaped Molecules. *Liq. Cryst.* **2000**, *27*, 429-436.
30. Shen, D.; Pegenau, A.; Diele, S.; Wirth, I.; Tschierske, C. Molecular Design of Non-Chiral Bent-Core Liquid Crystals with Antiferroelectric Properties. *J. Am. Chem. Soc.* 2000, 122, 1593-1601.

31. Thisayukta, J.; Nakayama, Y.; Kawauchi, H.; Takezoe, H.; Wantanabe, J. Distinct Formation of a Chiral Smectic Phase in Achiral Banana-Shaped Molecules with a Central Core Based on a 2,7-Dihydroxynaphthalene Unit. *J. Am. Chem. Soc.* 2000, 122, 7441-7448.

32. Heppke, G.; Parghi, D.D.; Sawade, H. Novel Sulphur-Containing Banana-Shaped Liquid Crystal Molecules. *Liq. Cryst.* 2000, 27, 313-320.

33. Kovalenko, L.; Weissflog, W.; Granda, S.; Diele, S.; Pelzl, G.; Wirth, I. Dimorphism SmA-B2 in Bent-Core Mesogens with Perfluorinated Terminal Chains. *Liq. Cryst.* 2000, 27, 683-687.

34. Thisayukta, J.; Nakayama, Y.; Kawauchi, H.; Wantanabe, J. Effect of Chemical Structure on the Liquid Crystallinity of Banana-Shaped Molecules. *Liq. Cryst.* 2000, 27, 1129-1135.

35. Fatiadi, A.J. Active Manganese Dioxide Oxidation in Organic Chemistry. *Synthesis* 1976, 65-104.

36. Belloni, M.; Manickam, M.; Preece, J. A. Towards Banana-Shaped Liquid Crystals Incorporating Carbazole. *Ferroelectrics* 2002, 276, 103-138.

37. Bedel, J.P.; Rouillon, J.C.; Marcerou, J.P.; Laguerre, M.; Achard, M.F.; Nguyen, H.T. Novel Mesophases in Fluorine Substituted Banana-Shaped Mesogens. *Liq. Cryst.* 2000, 27, 1411-1421.

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