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Octasubstituted dibenzochrysenes: discotic liquid crystals with a twisted core

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Octasubstituted dibenzochrysenes: discotic liquid crystals with a twisted core

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Octafunctionalised dibenzochrysenes are prepared in order to study the liquid crystalline properties that have chiral and achiral peripheral aliphatic chains. The syntheses of dibenzochrysene derivatives are achieved by a conventional method that has been developed recently. The achiral derivatives that have long peripheral aliphatic chains exhibit hexagonal and rectangular columnar mesophases over a wide thermal range, whereas those with short chains exhibit only hexagonal or more ordered (not identified) columnar phases, such as the columnar plastic. The chiral derivates exhibit only the hexagonal columnar mesophase. The nature of these mesophases is investigated by polarising optical microscopy and X-ray diffraction studies.

Keywords: dibenzochrysene; discotic liquid crystal; columnar; oxidative coupling

1. Introduction

There is considerable interest in the development of novel polycyclic aromatic hydrocarbon or benzonoid aromatic cores having peripheral aliphatic substitutions (*1*, *2*). These aromatic cores represent a class of organic functional materials (*3–5*). Significant attention has been paid to such molecules. They are self-organised into long columnar stacks and packed in a two-dimensional hexagonal lattice (*6–8*). A π-system formed by aromatic cores creates a one-dimensional pathway for charge transport along the axis of the column. The resulting 'molecular wires' exhibit one-dimensional charge transport properties, which make them promising functional materials (*9*, *10*). These molecules also hold the potential to serve as building blocks for the preparation of functional electronic and optoelectronic devices.

Previously, we have reported that dibenzochrysene (DBC) ether derivatives exhibit a columnar mesophase in the presence of a charge transfer (C-T) complex with 2,4,7-trinitrofluoren-9-one (TNF). In the absence of that C-T additive, these derivatives are non-mesomorphic (*11*, *12*). Our continuing interest in the design and synthesis of new discotics, which are of fundamental importance to organic materials science, prompted the synthesis of octasubstituted DBCs. Thus, by following a reported method (we have developed a new synthetic route to prepare the octamethoxydibenzochrysene, which is the key precursor to achieve the liquid crystalline dibenzochrysene core. We found that a quite similar method has been used to prepare octamethoxydibenzochrysene (*13*)), we have synthesised octasubstituted DBC derivatives exhibiting the liquid crystalline properties. To the best of our knowledge these are the first examples of liquid crystalline octasubstituted DBC derivatives.

2. Results and discussion

2.1 *Samples and synthesis scheme*

We synthesised DBC compounds with different peripheral aliphatic chain lengths. The molecular structures and synthesis scheme are shown in Scheme 1. The final compound **5** has five homologues **5a**, **5b**, **5c**, **5d** and **5e** with different lengths of achiral peripheral aliphatic chains. Homologues with chiral peripheral aliphatic chains, **5f** and **5g**, were also synthesised.

2.2 *Mesomorphism*

The microscopic textural observations were carried out using polarising optical microscopy (POM) and the enthalpies associated with different transitions were determined using differential scanning calorimetry (DSC). In this study, we have synthesised five new achiral and two chiral DBC derivatives. All of the derivatives exhibit the liquid crystalline phases. The transition temperatures and associated enthalpies obtained from DSC thermograms are given in Table 1.

All of the compounds are thermally very stable as confirmed by the reproducibility of thermograms on several heating and cooling cycles. In some cases, the solvent crystallised and melt crystallised solids show different melting points. This may be due to different crystal forms obtained during the two different processes. Compound **5a** shows the $\mathrm{Col_x}$ (appears like $\mathrm{Col_p}$), whereas **5b** shows the $\mathrm{Col_h}$ mesophase. On

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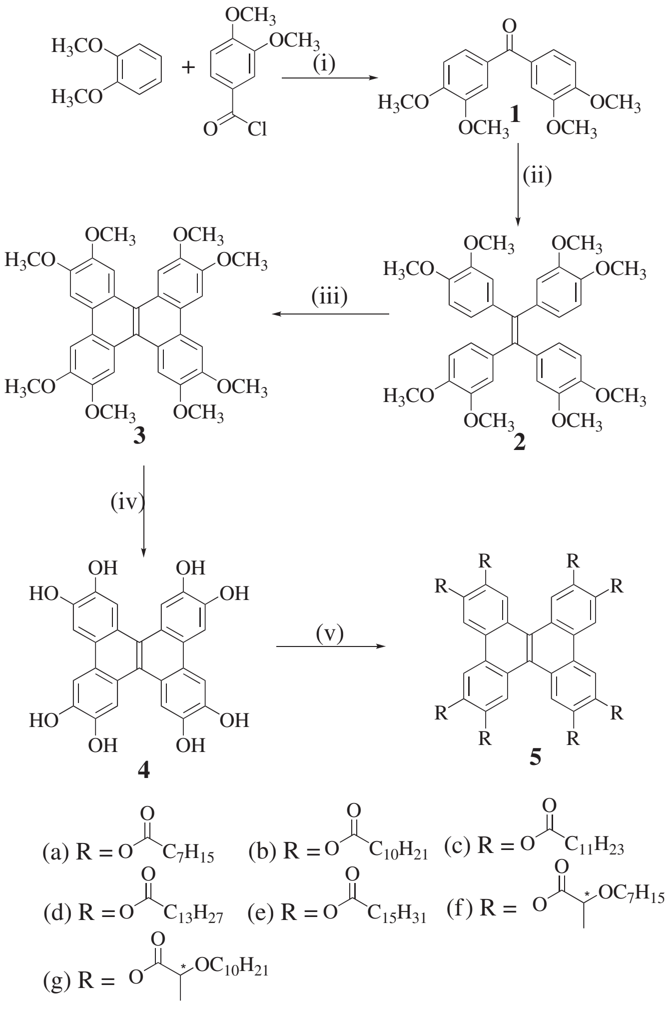

Reaction reagents and conditions:
(i) $AlCl_3$, CS_2, 40 ºC, 10 h; (ii) $TiCl_4$, Zn, Py., CH_2Cl_2,THF, 70 ºC, 15 h ; (iii) $FeCl_3$, CH_2Cl_2, 30 min. r.t. ; (iv) BBr_3, CH_2Cl_2, 0ºC-r.t., 10 h; (v) RCOCl, Py., Zn, THF, 80 ºC, 20 h

Scheme 1. The synthesis of octafunctionalised DBCs.

further increasing the peripheral aliphatic chains, compounds **5c** and **5d** exhibit the Col_r phase in addition to the Col_h mesophase. Compound **5e**, having very long peripheral chains, shows two unknown mesophases (M and M_1) in addition to the Col_h and Col_r mesophases. Further works are under progress to confirm the nature of these unknown mesophases. Note that discotic molecules with C16 chain length in periphery have rarely been reported. The chiral compounds, **5f** and **5g**, show the Col_h mesophase. The isotropic temperature decreased drastically in these chiral compounds, due to the branching effect.

Compound **5a,** on cooling from the isotropic liquid, forms a dendritic texture. From the texture, this phase appears like a Col_p mesophase, as shown in Figure 1(a). Note that a similar characteristic texture has also been reported for several other discotic cores (*14*, *15*). Compound **5c** exhibits a mosaic texture with some domains of fan-like and/or petal-like features, characteristic of the Col_h phase on cooling from the isotropic phase, as shown in Figure 1(b). Compound **5d**, on cooling from the isotropic phase, shows the rod-like texture characteristic of the Col_r mesophase, as shown in Figure 1(c). A mosaic texture of the Col_h phase of compound **5f** (chiral derivative) was observed on cooling from the isotropic liquid (see Figure 1(d)). The use of peripheral branched chains in discotic liquid crystals reduces the transition temperatures and often the type of mesophases formed is not affected (*16–20*).

Table 1. Thermal behaviour of octasubstituted DBCs. Phase transition temperatures (°C) and enthalpies [in parenthesis, Jg^{-1}] of compound **5**. The values were determined in the second or higher heating and cooling cycle of DSC scans. The phase identification was made by POM and X-ray diffraction (see Table 2).

Compound	Heating scan	Cooling scan
5a	Col_x 233.7 [24.3] I	I 229.6 [20.4] Col_x
5b	Col_h 219.7 [10.2] I	I 215.0 [7.3] Col_h
5c	Col_r 201.0 [1.6] Col_h 215.9 [11.8] I	I 213.9 [11.6] Col_h 198.4 [1.5] Col_r
5d	Cr 40.9 [21.5] Col_r 185.2 [0.7] Col_h 209.2 [10.8] I	I 206.2 [9.8] Col_h 180.9 [0.6] Col_r 35.8 [19.7] Cr
5e	M 58.1 [20.7] Col_h 199.7 [7.6] I	I 196.8 [7.7] Col_h 50.2 [27.0] M 45 [4.8] Col_r 34.6 [18.4] M_1
5f	Col_h 104.2 [14.6] I	I 95.3 [14.9] Col_h
5g	Col_h 100.2 [15.2] I	I 92.1 [16.3] Col_h

Cr – crystal; Col_x – unknown columnar; Col_h – hexagonal columnar; Col_r – rectangular columnar; M_1 and M – mesophase yet to confirm; I – isotropic.

2.3 X-ray diffraction study

The results of X-ray investigations of the columnar mesophases of compounds **5a, 5b, 5e and 5g** are summarised in Table 2. Figure 2(a) shows the X-ray diffraction profile as a function of 2θ for compound **5b**. A sharp reflection in the small-angle regime corresponds to the disc diameter. In addition, a weak reflection (see arrow in inset) can also be seen. These reflections are attributed to (10) and (11) reflections, d_{10} and d_{11}, respectively, because of the characteristic ratio ($1{:}1/3^{1/2}$) for the (10) and (11) reflections of a two-dimensional hexagonal lattice. The wide-angle regime shows a broad reflection, which corresponds to the molten alkyl chains. The reflection corresponding to the core-core was not observed, partly because of the molecular disorder in the mesophase due the propeller structure of the DBC core.

Figure 2(b) shows the X-ray diffraction profile as a function of 2θ for compound **5e**. At a higher temperature the reflection corresponds to the hexagonal

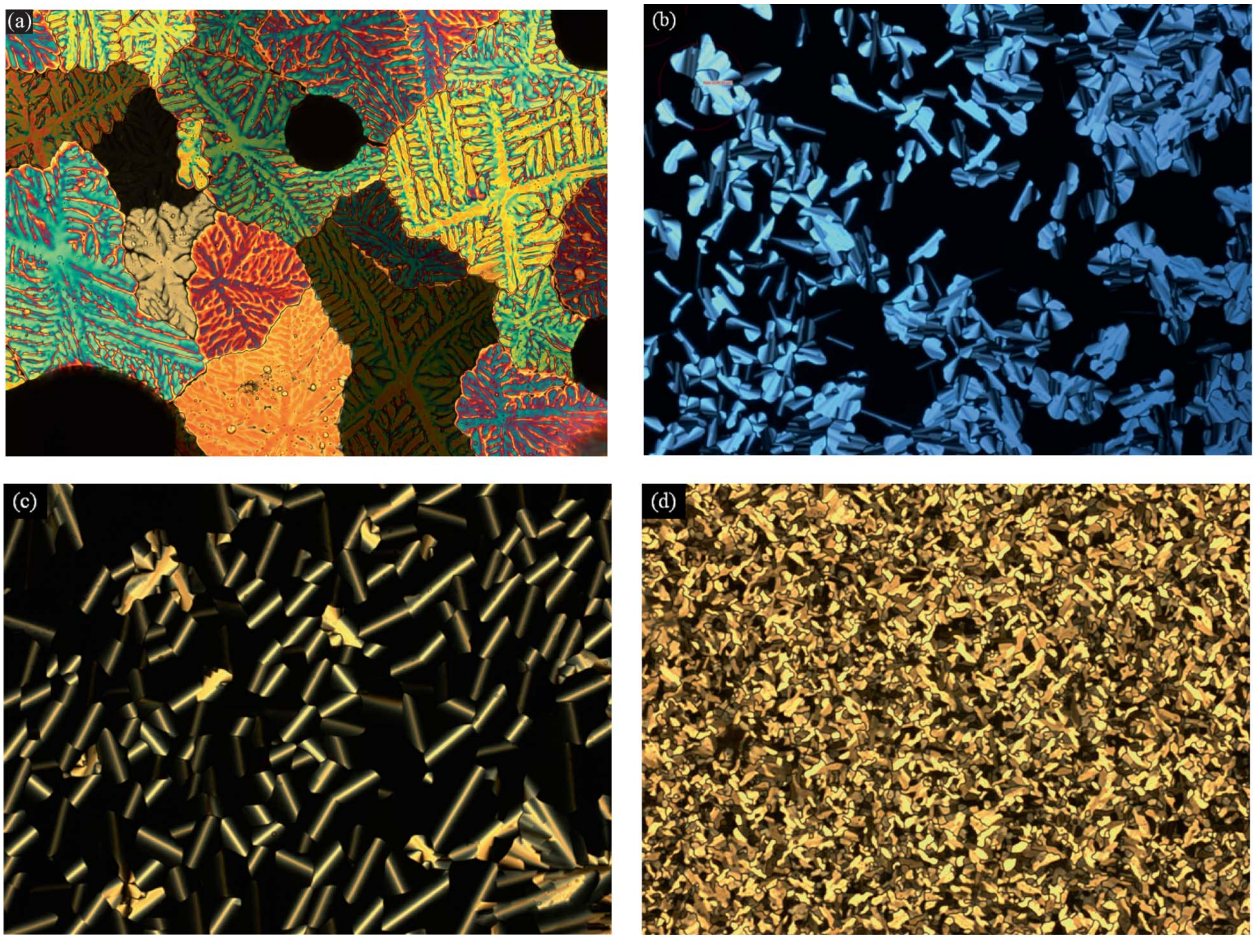

Figure 1. The mesophase textures observed by POM (magnification ×200): (a) Col_x phase at room temperature, obtained on cooling the isotropic liquid of compound **5a**; (b) Col_h phase at 200°C, obtained on cooling of compound **5c**; (c) Col_r phase at 40°C, obtained on cooling of compound **5d**; (d) Col_h phase at room temperature, obtained on cooling of compound **5g**.

Table 2. X-ray diffraction data of the columnar mesophases for compound **5**.

Compound	Mesophase and parameters	d_{obs}[a] [Å]	*hk*[b]	d_{calc}[a] [Å]
5a	Col_x, 80°C	21.9	(10)	22.0
		5.5		
		4.6		
		2.9		
5b	Col_h, 40°C	24.9	(10)	25.2
		14.9	(11)	14.9
		4.9		
5e	Col_r, 40°C	40.5	(20)	40.5
		31.6	(11)	31.5
		25.9	(21)	25.8
		19.8	(40)	19.8
		15.9	(22)	15.8
	Col_h, 170°C	31.6	(10)	31.5
		17.8	(11)	17.9
5g	Col_h, 80°C	29.5	(10)	30.2
		17.1	(11)	17.4
		14.8	(20)	15.0
		11.2	(21)	11.4

[a]Observed and calculated diffraction spacings; [b]Miller indices.

lattice, whereas the data recorded at 40°C is consistent with a rectangular lattice. The (10) peak of the hexagonal lattice splits into the (20) and (11) reflections of the rectangular lattice with the lattice constants: $a = 81$ Å, $b = 34.3$ Å. The indices of the remaining higher order reflections are listed in Table 2. The X-ray pattern of the chiral derivative (**5g**) was obtained at higher and lower temperatures. Two small-angle reflections correspond to d_{10} and d_{11} of the hexagonal lattice. Together with two other higher order reflections (Table 2), four peaks correspond to the characteristic ratio of $1:1/3^{1/2}:1/2:1/7^{1/2}$ for the *d* spacing of the (10), (11), (20) and (21) reflections of a two-dimensional hexagonal lattice are obtained in the small-angle regime. The X-ray study shows that the achiral derivatives exhibit the disordered hexagonal columnar mesophase, whereas chiral derivatives exhibit the ordered hexagonal columnar mesophase.

The MM2 energy minimisation of the DBCs core shows the twisted structure. The top view suggests a flat molecule, which was reported by Kumar and Varshney (*12*). However, the side view clearly shows

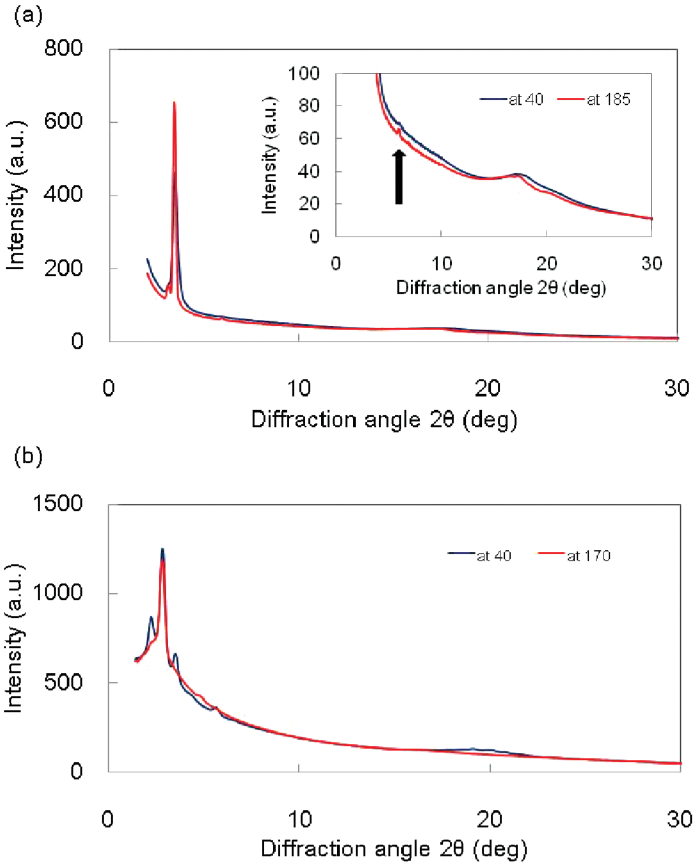

Figure 2. (a) X-ray diffraction patterns of the Col_h phase of compound **5b** at 40 (black) and 185°C (red). (b) X-ray diffraction intensity versus 2θ in the Col_r phase of compound **5e** at 40 (black) and 170°C (red).

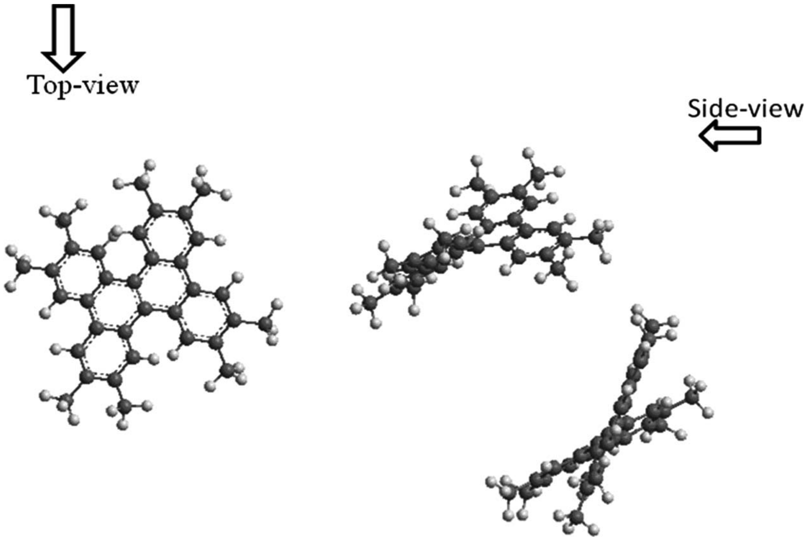

Figure 3. MM2 energy-minimised structures of the octasubstituted dibenzochrysene molecule display a planar core on viewing from the top (left panel) and a propeller on rotating 90° from vertical (or side view) (right panel). The peripheral chains are eliminated for a clear view.

the propeller structure of the molecules (Figure 3). The calculated structure is consistent with the reported X-ray crystallographic data (*21*). The propeller structure of the core could be the reason that the octasubstituted ether derivatives are non-mesogenic. Further theoretical and experimental studies are under progress to confirm the twisted molecular structure of this discotic core.

3. Experimental

3.1 General

Commercially available chemicals and solvents were obtained and were used without further purification. All of the reactions were carried out under an argon atmosphere. The tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were refluxed over sodium metal (Na) and calcium hydride (CaH), respectively, under the argon atmosphere. Thin layer chromatography (TLC) was performed on a Merck, Kieselgel 60, F_{254}. ^1H and ^{13}C spectra were recorded on a Bruker 400 MHz spectrometer. The matrix-assisted laser desorption/ionization (MALDI) time-of-flight (TOF) mass spectra were recorded on a Kratos personal computer (PC) Axima CFR. The transition temperatures were determined by Perkin Elmer differential scanning calorimeter Diamond series. Peak temperatures observed in the heating and cooling runs at the rate of 5°C min^{-1} are reported. The optical textures were observed using an Olympus BX51 polarising optical microscope equipped with a Mettler FP82HT hot stage. The X-ray diffraction data were obtained by a Rigaku RU-200 X-ray system (CuKα) with a temperature control unit.

3.2 Synthesis of tetramethoxybenzophenone

(1): To a solution of 3g (0.2 mol) of veratrole and 3.2 g (0.024 mol) $AlCl_3$ in 20 ml dry CS_2, was added, in portions at 0°, a solution of 4.3g (0.2 mol) of 3,4-dimethoxybenzoyl chloride in 10 ml CH_2Cl_2 and the resulting mixture was refluxed for 15 h. After cooling to room temperature, this was poured into ice cold water and extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4. The solvent was removed under vacuum and the residue was purified by recrystallisation from methanol. Yield: 4.6 g (70%) white solid. M.p. 147.1°; ν_{max} / cm^{-1}: 2935, 2838, 1642, 1579, 1595, 1514, 1462, 1416, 1266, 1171, 1136, 1124, 1023; ^1H NMR: $\delta = 7.4$ (d, 2H, $J = 2$), 7.39 (d, 1H, $J = 2$), 7.37 (d, 1H, $J = 2$), 6.92 (s, 1H), 6.90 (s, 1H), 3.97 (s, 6H), 3.95 (s, 6H).

3.3 Synthesis of tetrakis(3,4-dimethoxyphenyl)ethene

(2): The method of McMurry Coupling was followed as reported in the literature (*22*). M.p. 169.8°; ν_{max} / cm^{-1}:2936, 2834, 1599, 1511, 1462, 1410, 1241, 1138, 1027; ^1H NMR: $\delta = 6.6$ (m, 12H), 3.82 (s, 12H), 3.53 (s, 12H).

3.4 Synthesis of octamethoxydibenzochrysene

(3): Compound **2** (1 g, 0.017 mol) was dissolved in CH_2Cl_2 (15 ml) and Iron(III)chloride (2.3 g 0.014 mol) was added in portions under the argon atmosphere. The reaction mixture was vigorously stirred at room temperature and the reaction was monitored by TLC. The reaction was completed in 1.2 h. This was quenched with chilled MeOH, water was added and the mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4. The solvent was evaporated and the reddish solid obtained was purified by recrystallisation in MeOH to afford compound **3** (0.4 g, yield = 40%). M.p. = >250°; ν_{max} / cm^{-1}: 2932, 1612, 1509, 1462, 1416, 1259, 1191, 1041, 1010; ^{1}H NMR: δ = 8.2 (s, 4H), 7.88 (s, 4H), 4.17 (s, 12H), 4.01(s, 12H).

3.5 Synthesis of octahydroxydibenzochrysene

(4): To a solution of compound **3** (0.4 g, 0.0007 mol) in anhydrous $CH_2Cl_{2.}$ (1.6 g, 0.006 mol), boron tribromide (BBr_3) (Aldrich # 202207) solution in 10 ml CH_2Cl_2 was added dropwise at –60° with the help of a syringe. The resulting mixture was stirred at –60° for 2 h and then stirred at room temperature for 15 h. The reaction mixture was quenched with chilled water and extracted with $CH_2Cl_{2.}$ The solvent was evaporated and the product obtained (0.3 g, yield = 90%), which was sufficiently pure as indicated by its NMR spectra, was used for a further esterification reaction. Fourier transform infrared (FT-IR) (KBr): ν = 3350, 1515, 1451, 1378, 1278, 1144 cm^{-1}. ^{1}H-NMR (400 MHz, CD_3OH): δ (ppm) = 8.07 (s, 4H), 7.8 (s, 4H), 4.86 (s, 8H).

3.6 General procedure for the preparation of octasubstituted DBCs

(5): To a solution of 0.1 g (0.0002 mol) octahydroxydibenzochrysene (**4**), zinc dust (0.002 mol) and dry pyridine (0.5 ml) was added dropwise, along with alkanoyl chloride or alkoxypropionyl chloride (0.0026 mol) in 10 ml dry THF at 0°C and the mixture was refluxed for 18 h . After cooling to room temperature, the zinc was removed by filtration and the filtrate was extracted with CH_2Cl_2. The organic layer was dried over Na_2SO_4 and evaporated. The crude product was purified by flash chromatography.

5a: Yield = 70%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4H), 8.31 (s, 4H), 2.66–2.58 (m, 16H), 1.89–1.75 (m, 16H), 1.47–1.31 (m, 58H), 0.89 (q, 24H, J = 7.7). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.2, 141.6, 123.2, 117.9, 34.1, 31.6, 29.1, 28.9, 24.8, 22.6, 14.0. MS (MALDI-TOF): calcd. for $C_{90}H_{128}O_{16}$ $[M]^+$ 1464, found $[M+Na]^+$ 1488. FT-IR (KBr): ν = 2956, 2926, 2855, 1759, 1502, 1465, 1426, 1377, 1263, 1148 cm^{-1}.

5b: Yield = 65%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4H), 8.31 (s, 4H), 2.66–2.58 (m, 16H), 1.89–1.75 (m, 16H), 1.47–1.31 (m, 112H), 0.89 (m, 24H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.2, 141.5, 123.1, 117.8, 34.2, 31.5, 29.0, 28.7, 24.8, 22.6, 14.0. MS (MALDI-TOF): calcd. for $C_{114}H_{176}O_{16}$ $[M]^+$ 1800, found $[M+Na]^+$ 1823.

5c: Yield = 65%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4H), 8.31 (s, 4H), 2.66–2.58 (m, 16H), 1.89–1.75 (m, 16H), 1.47–1.31 (m, 112H), 0.89 (m, 24H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.2, 171.0, 141.6, 141.4, 128.5, 127.1, 126.7, 123.2, 117.9, 34.2, 31.9, 29.6, 29.5, 29.2, 24.9, 22.0, 14.0. MS (MALDI-TOF): calcd. for $C_{122}H_{192}O_{16}$ $[M]^+$ 1912, found $[M+Na]^+$ 1935.

5d: Yield = 52%, white solid, ^{1}H-NMR (400MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4H), 8.31 (s, 4H), 2.66–2.58 (m, 16H), 1.89–1.75 (m, 16H), 1.47–1.26 (m, 160H), 0.89 (t, 24H, J = 6). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.2, 171.0, 141.6, 141.5, 128.5, 127.1, 126.7, 123.2, 117.9, 34.2, 31.9, 29.7, 29.5, 29.3, 29.2, 25.0, 24.9, 22.6, 14.0. MS (MALDI-TOF): calcd. for $C_{138}H_{224}O_{16}$ $[M]^+$ 2136, found $[M+Na]^+$ 2159.

5e: Yield = 45%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.45 (s, 4H), 8.31 (s, 4H), 2.66–2.58 (m, 16H), 1.89–1.75 (m, 16H), 1.47–1.31 (m, 192H), 0.89 (t, 24H, J = 8). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.0, 170.9, 141.6, 128.5, 127.2, 123.2, 117.9, 34.2, 31.9, 29.7, 29.3, 24.9, 22.0, 14.0. MS (MALDI-TOF): calcd. for $C_{154}H_{256}O_{16}$ $[M]^+$ 2360, found $[M+Na]^+$ 2383.

5f: Yield = 35%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.53 (s, 4H), 8.39 (s, 4H), 4.32–4.21 (m, 8H), 3.83–3.71 (m, 8H), 3.57–3.43 (m, 8H), 1.67 (d, 20H, J = 6.8), 1.63 (d, 20H, J = 9), 1.4–1.22 (m, 76H), 0.9–0.83 (m, 24H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.6, 170.9, 141.8, 141.2, 128.5, 127.1, 123.5, 117.7, 74.9, 74.8, 71.0, 70.8, 31.8, 30.9, 29.8, 29.6, 29.3, 26.0, 22.6, 18.9, 14.0. MS (MALDI-TOF): calcd. for $C_{106}H_{160}O_{24}$ $[M]^+$ 1816, found $[M+Na]^+$ 1839.

5g: Yield = 40%, white solid, ^{1}H-NMR (400 MHz, $CDCl_3$): δ (ppm) = 8.5 (s, 4H), 8.4 (s, 4H), 4.32–4.21 (m, 8H), 3.83–3.71 (m, 8H), 3.57–3.43 (m, 8H), 1.67 (d, 20H, J = 6.9), 1.63 (d, 20H, J = 6.8), 1.4–1.22 (m, 112H), 0.9–0.83 (m, 24H). ^{13}C-NMR (100 MHz, $CDCl_3$): δ (ppm) = 171.2, 170.9, 141.2, 141.0, 128.5, 127.1, 123.5, 117.7, 74.9, 74.8, 70.9, 70.8, 31.8, 30.9, 29.8, 29.6, 29.3, 26.0, 22.6, 18.9, 14.0. MS (MALDI-TOF): calcd. for $C_{130}H_{208}O_{24}$ $[M]^+$ 2152, found $[M+Na]^+$ 2175.

4. Conclusion

A series of chiral and achiral octafunctionalised DBCs were prepared by the facile method and their liquid crystalline properties were studied. The lowest homologue of the achiral series exhibits the unidentified columnar mesophase (Col_x). The next lowest derivative, having the longer peripheral aliphatic chains, exhibits the hexagonal columnar phase and on further increasing the length of the peripheral aliphatic chains, a rectangular columnar phase is induced. Compound **5e**, having the very long (compared to the other known polyaromatic discotic core) peripheral aliphatic chains, exhibits the two unknown mesophases in addition to the hexagonal and rectangular columnar mesophases. Detailed investigations of the electro-optical, photophysical and electronic properties of this mesophase sequence are presently in progress.

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