

Dibenzo[*a,c*]phenazine with six-long alkoxy chains to probe optimization of mesogenic behavior

Chi Wi Ong,^{*a} Ja-Yi Hwang,^a Mei-Chun Tzeng,^a Su-Chih Liao,^a Hsiu-Fu Hsu^b and Tsu-Hsin Chang^a

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New hexaalkoxydibenzo[*a,c*]phenazines (**HDBPs**) with six-carbon long chains have been prepared, and their mesogenic behavior investigated. The incorporation of six peripheral alkoxy groups onto the larger, dipolar core bearing nitrogen atoms showed interesting thermal properties. The crystal-to-mesophase transitions for the **HDBPs** (K–col) are similar to the triphenylenes, but the clearing temperatures (Col–I) are shifted upwards by approx. 60 °C. **HDBP** therefore possesses stable hexagonal mesophases in a fairly broad temperature range and form homeotropically aligned films.

Introduction

The liquid crystal (LC) properties of disc-shaped molecules have been of considerable interest ever since their discovery by Chandrasekhar¹ in 1977. The number of known discotic LCs is growing continuously;² and their columnar arrangement is especially promising for the anisotropic transport of charge carriers along the columns. Discotic LCs are being recognized for their potential applications in photovoltaic devices, field effect transistors (FETs), light emitting diodes (LEDs) and other molecular electronics.³ Some of the most prominent discotic LCs range from the widely-investigated triphenylenes,⁴ to porphyrins,⁵ phthalocyanines,⁵ hexaazatriphenylenes,^{6–8} perylenes,⁹ dibenzopyrenes,¹⁰ hexabenzocoronenes,^{11,12} dibenzoquinoxalines¹³ and dibenzo[*a,c*]phenazine.¹⁴

The dibenzo[*a,c*]phenazine core possesses a phenanthrene ring fused to pyrazine, and this gives rise to a molecular dipole moment. The dipole moment contributes to the preferential antiparallel orientation of adjacent molecules within the column. Recently, Williams *et al.*¹⁴ reported low-symmetry tetraalkoxydibenzo[*a,c*]phenazines with electron withdrawing groups at the pyrazine moiety exhibit liquid crystalline properties by forming fairly symmetrical columns through this kind of interaction.¹⁴ However, electron-donating methyl and methoxy groups at the pyrazine moiety of tetraalkoxydibenzo[*a,c*]phenazines are nonmesogenic.¹⁴

This report prompted us to disclose results of our own work in this area, which utilises the more symmetrical hexaalkoxydibenzo[*a,c*]phenazines with long carbon chains, shown by the general formula **HDBP**, to obtain mesogenic properties. These new **HDBP** with six-carbon long alkoxy chains can provide further insight into the relative importance of the peripheral side-chains in enforcing the propensity of these compounds to self assemble into columnar liquid crystal phases. The new

HDBPs differs from the well-known triphenylenes in that they have; (i) a larger core, (ii) an unsymmetrical core, (iii) a dipole moment within the core. Furthermore, it will be interesting to compare the symmetrically substituted **HDBP** with the asymmetric dibenzophenazine possessing two methoxy groups and four hexyloxy groups, which is not mesogenic. Clearly, the unsymmetrical phenazine core and the symmetrical peripheral long alkyl chain may be expected to affect the packing of molecules within the mesophase. In this regard, we may expect the unsymmetrical core to increase intermolecular lateral slippage; while the dipole–dipole interaction contributes to the preferential antiparallel orientation of the adjacent molecules within the column to enhance intracolumnar π – π interactions. This work might lead to the discovery of new hexaalkoxydibenzo[*a,c*]phenazines (**HDBP**), discotic liquid crystals with a useful mesogenic range, thereby improving their processing characteristics for applications.

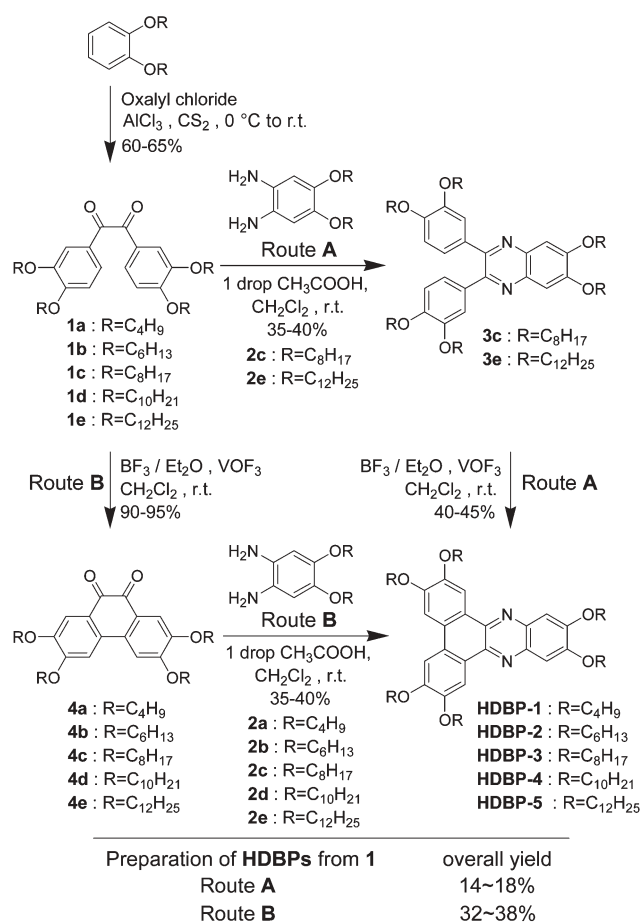
Results and discussion

Hexaalkoxydibenzo[*a,c*]phenazine (**HDBP**) derivatives have been synthesised directly from the condensation of 1,2-diamines with benzils followed by oxidative cyclization (route A); or from the condensation of 1,2-diamines with phenanthrene-9,10-diones (route B).^{13,14} While preparation of liquid crystalline materials is often (but not always) simple, their purification is usually difficult and tedious. As such, both routes were examined.

Our initial approach to synthesise hexaalkoxydibenzo[*a,c*]phenazines (**HDBP**) is outlined in (Scheme 1, route A). The tetraalkoxybenzils **1a–e** were synthesised from the reaction of 1,2-bisalkoxybenzene (from the alkylation of catechol in >90% yield) and oxalyl chloride in 60–65% yield in accordance to the procedure described by Wegner.¹⁵ The above protocol to synthesise symmetrical tetraalkoxybenzils is greatly superior; Williams^{14,16} has previously used a benzoin condensation route reported by Wenz¹⁶ which gave an average overall yield of 29% in four steps. The tetraalkoxybenzils **1a–e** were then condensed with 1,2-bisalkoxy-4,5-diaminobenzenes **2** previously prepared in our laboratory⁷ to furnish the quinoxaline

^aDepartment of Chemistry, National Sun Yat Sen University, Kaohsiung 80424, Taiwan E-mail: cong@mail.nsysu.edu.tw; Fax: +886 7 5253908; Tel: +886 7 5252000-3923

^bDepartment of Chemistry, Tamkang University, Tamsui 25137, Taiwan E-mail: hhsu@mail.tku.edu.tw; Fax: +886 2 26209924; Tel: +886 2 26215656



Scheme 1 The synthesis of hexaalkoxydibenzo[*a,c*]phenazines (HDBPs)

derivatives. A variety of oxidants such as palladium(II) acetate, FeCl₃, thallium(III) oxide and vanadium(V) oxyfluoride have been studied for the conversion of 3,3',4,4'-tetraalkoxy-substituted to the dibenzoquinoxaline. The best results were achieved, however, with VOF₃, which cleanly oxidises benzils to phenanthrene-9,10-diones. Thus, we choose to use VOF₃ for the oxidative cyclization, and this furnishes hexaalkoxydibenzo[*a,c*]phenazines (HDBPs) in excellent yield. The product obtained has to be rigorously purified due to its close resemblance to the quinoxalines starting material. Although we were able to obtain pure HDBPs by column chromatography, however, repeating separation was required due to poor resolution, and much remained as a mixture. In spite of requiring tedious separation, this route has the advantage of enabling us to study the mesogenic properties for both the uncyclized 2,3-bis(3,4-dialkoxyphenyl)-6,7-dialkoxyquinoxaline **3** and cyclised hexaalkoxydibenzo[*a,c*]phenazine (HDBP) derivatives.

Given the low overall level of yield for the synthesis of HDBPs from route A (14–18% from benzils), we chose to focus upon an alternative synthetic route that utilised tetraalkoxyphenanthrene-9,10-diones **4a–e**^{15,17,18} as starting materials. Tetraalkoxyphenanthrene-9,10-diones were synthesized from the oxidative cyclization of the tetraalkoxybenzils **1a–e** with VOF₃¹⁵ cleanly in excellent yield (90–95%).

Condensation of the tetraalkoxyphenanthrene-9,10-diones with 1,2-bisalkoxy-4,5-diaminobenzenes furnished hexaalkoxydibenzo[*a,c*]phenazines (**HDBP-1–5**) in yields ranging from 35–40%, and the problem of purification was rectified. In all cases, the main product were obtained readily. Thus, route B allowed us to synthesise the key compound in a much higher overall yield (32–38%) from benzils.

The phase-forming properties of 2,3-bis(3,4-dialkoxyphenyl)-6,7-dialkoxyquinoxaline **3** and hexaalkoxydibenzo[*a,c*]phenazine (HDBP) derivatives were investigated using polarized optical microscopy (POM), differential scanning calorimetry (DSC) and variable temperature X-ray diffraction (XRD) and the results summarized in (Fig. 1), (Table 1) and (Table 2). The 2,3-bis(3,4-dioctyloxyphenyl)-6,7-dioctyloxyquinoxaline, **3c**, was found to be non-mesogenic, melting directly from the crystalline solid to isotropic liquid. The presence of six octyloxy peripheral chains cannot overcome the non-planarity of the unfused aromatic rings in 2,3-bis(3,4-dialkoxyphenyl)-6,7-dialkoxyquinoxaline, thus suppressed mesophase formation. Even with the use of a dodecyloxy side chain, **3e**, this did not lead to the formation of a mesophase.

Mesogenic behavior is observed for all the synthesised hexaalkoxydibenzo[*a,c*]phenazine derivatives with long alkoxy chains (**HDBP-1**: R = C₄H₉, **HDBP-2**: R = C₆H₁₃, **HDBP-3**: R = C₈H₁₇, **HDBP-4**: R = C₁₀H₂₁, and **HDBP-5**: R = C₁₂H₂₅). Thus, planarization of the discogen core has led to favorable mesophase formation. A typical birefringent fan texture of the columnar mesophase was observed by POM (Fig. 1f, without cover glass). All other liquid crystalline members of the series also exhibit similar texture, confirming the columnar nature of the mesophase. Most of the compounds also shows large domains of homeotropically aligned region, where columns are perpendicular to the glass plane, indicating the planar molecules packed parallel to the substrate surface (Fig. 1a–e, with cover glass). Geerts has recently illustrated that the confinement imposed on the film between two glass plates plays an important role for homeotropic alignment.¹⁹ Examination of these compounds by DSC revealed that **HDBP-1**, **HDBP-2** and **HDBP-5** undergo two phase transitions upon heating; which were identified by POM as crystal-to-liquid crystal and liquid crystal-to-isotropic liquid transitions (Fig. 2a: DSC of **HDBP-1**). The remaining compounds, **HDBP-3** and **HDBP-4**, each undergo three phase transitions (Fig. 2b: DSC of **HDBP-3**). We were not able to confirm the identity of the first liquid crystal phase having a very narrow phase range, while the broader second liquid crystal phase were easily identified by POM. X-ray diffraction studies of **HDBP-1**, **2**, **3**, **4** and **5** confirmed the mesophase assignment made by POM and DSC. The pattern shows a strong maximum in the low angle region that corresponds to the (100) reflection from the two dimensional hexagonal lattice with a lattice constant *a* in Å. Other two small peaks can be indexed to the (110) and (200) reflections, confirming the Col_h assignment (Fig. 3: XRD pattern of **HDBP-3**). At the wide-angle region, two diffuse scattering maxima were observed, corresponding to a distance of approximately 4.6 and 3.5 Å, typical of the interchain halo and intracolumnar π–π stacking distances, respectively. We have demonstrated that by introducing six alkoxy peripheral chains at the

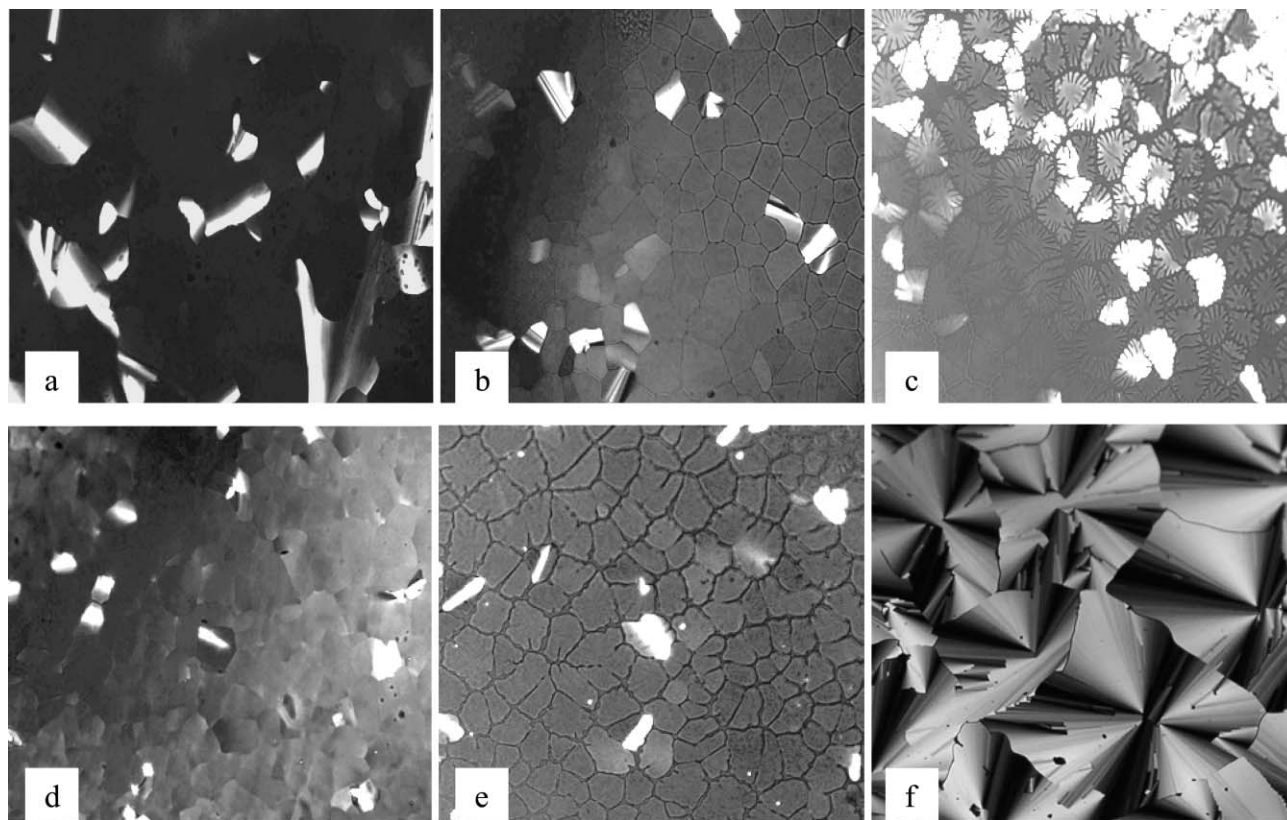


Fig. 1 The texture of (a) **HDBP-1** at 200 °C, $\times 100$, (b) **HDBP-2** at 150 °C, $\times 100$, (c) **HDBP-3** at 150 °C, $\times 100$, (d) **HDBP-4** at 110 °C, $\times 100$, (e) **HDBP-5** at 118 °C, $\times 100$, with cover glass (homeotropic), (f) **HDBP-5** at 118 °C, $\times 100$, without cover glass.

dibenzo[*a,c*]phenazine core can enforced the formation of liquid crystalline phases.

We would like to stress here that the crystal to mesophase transition temperature (T_{K-Col}) for **HDBP-1–5** (Table 1) is much lower, as compared to the reported tetraalkoxy-dibenzo[*a,c*]phenazines with electron withdrawing groups.¹⁴ The unsymmetrical core can led to a less-efficient packing of the solid, and thus lowering the melting point. It is interesting to note that these melting points are similar to

those of the corresponding triphenylenes.^{1,20,21} The introduction of a larger core and a dipole moment within the core of **HDBP-1–5** does not affect the observed crystal to mesophase transition (K–Col). Furthermore, the intermolecular spacing of **HDBPs** with six peripheral alkoxy chains correlate well to those of the triphenylenes. Investigation by XRD also revealed that the intercolumnar spacing for **HDBPs** calculated from the *d*-spacing of the (100) reflection increases with increasing alkoxy chain length. Thus increasing the

Table 1 The phase behaviors of **HDBP-1, 2, 3, 4** and **5**. The transition temperatures (°C) and enthalpies (in parentheses/kJ mol^{−1}) were determined by DSC at 10 °C min^{−1}

Compound	Chain	Phase transition ^a
3c	R = C ₈ H ₁₇	K $\xrightleftharpoons[-2.5\text{ °C} (-30.71)]{5.3\text{ °C} (36.53)}$ I
3e	R = C ₁₂ H ₂₅	K $\xrightleftharpoons[-14.4\text{ °C} (-8.76)]{71.0\text{ °C} (96.48)}$ I
HDBP-1	R = C ₄ H ₉	K $\xrightleftharpoons[-95.8\text{ °C} (-36.40)]{137.7\text{ °C} (35.31)}$ Col _h $\xrightleftharpoons[-200.5\text{ °C} (-9.40)]{203.9\text{ °C} (9.50)}$ I
HCBP-2	R = C ₆ H ₁₃	K $\xrightleftharpoons[-27.8\text{ °C} (-23.41)]{69.9\text{ °C} (45.26)}$ Col _h $\xrightleftharpoons[-154.6\text{ °C} (-3.84)]{158.5\text{ °C} (3.89)}$ I
HCBP-3	R = C ₈ H ₁₇	K $\xrightleftharpoons[-30.1\text{ °C} (-42.55)]{64.5\text{ °C} (40.48)}$ Col _x $\xrightleftharpoons[-70.4\text{ °C} (1.75)]{30.1\text{ °C} (1.75)}$ Col _h $\xrightleftharpoons[-144.3\text{ °C} (-5.24)]{147.5\text{ °C} (5.40)}$ I
HCBP-4	R = C ₁₀ H ₂₁	K $\xrightleftharpoons[-29.5\text{ °C} (-51.52)]{55.2\text{ °C} (45.73)}$ Col _x $\xrightleftharpoons[-59.2\text{ °C} (2.07)]{29.5\text{ °C} (2.07)}$ Col _h $\xrightleftharpoons[-125.5\text{ °C} (-3.64)]{129.5\text{ °C} (3.79)}$ I
HCBP-5	R = C ₁₂ H ₂₅	K $\xrightleftharpoons[-36.3\text{ °C} (-66.54)]{56.5\text{ °C} (66.73)}$ Col _h $\xrightleftharpoons[-108.1\text{ °C} (-2.56)]{111.1\text{ °C} (2.75)}$ I

^a K, crystalline phase; Col_x, indistinct phase; Col_h, hexagonal columnar; I, isotropic.

Table 2 Variable-temperature XRD data for compounds **HDBP-1-5**

Compound	Chain	Temperature/°C	<i>d</i> -spacing/Å	Miller indices (<i>hkl</i>)	Lattice constants/Å
HDBP-1	R = C ₄ H ₉	190	16.95	(100)	<i>a</i> = 19.57
			9.72	(110)	
			8.44	(200)	
			6.39	(210)	
			4.60	Alkyl halo	
			3.53	Core-core	
HDBP-2	R = C ₆ H ₁₃	80	18.02	(100)	<i>a</i> = 20.81
			1.65	(110)	
			4.43	Alkyl halo	
			3.47	Core-core	
HDBP-3	R = C ₈ H ₁₇	80	20.98	(100)	<i>a</i> = 24.23
			12.14	(110)	
			10.46	(200)	
			7.95	(210)	
			4.56	Alkyl halo	
			3.47	Core-core	
HDBP-4	R = C ₁₀ H ₂₁	90	22.89	(100)	<i>a</i> = 26.43
			13.11	(110)	
			11.43	(200)	
			4.55	Alkyl halo	
			3.47	Core-core	
HDBP-5	R = C ₁₂ H ₂₅	100	24.86	(100)	<i>a</i> = 28.71
			14.44	(110)	
			12.54	(200)	
			4.78	Alkyl halo	
			3.55	Core-core	

alkoxy chain length leads to a lowering of the melting temperature.

While **HDBPs** have a lower clearing temperature compared to tetraalkoxydibenzo[*a,c*]phenazines with electron withdrawing groups,¹⁴ it is perhaps notable that they are shifted upwards by approx. 60 °C with respect to the triphenylene counterpart.^{1,20,21} This observation provides quantitative evidence that the non-cooperation of a larger core and a dipole moment within the core leads to a higher clearing

temperature. The lateral dipole of the mesogenic core can stabilises the columnar structure through an antiparallel packing of adjacent discs within the column, thus correlating to an anti-ferroelectric ordering of the lateral dipole along the column. Indeed, it has been reported that introducing a dipole through a peripheral substitution in triphenylenes caused an increase in the clearing temperature.²² This is also seen in tetraalkoxydibenzo[*a,c*]phenazines having electron withdrawing group at the pyrazine moiety to induce strong dipole, thus exhibit a high clearing temperature.¹⁴ It is apparent that the dipole-dipole interaction of adjacent molecules within the column can lead to an increase in the intracolumnar π - π interaction, and therefore stabilises the mesophase. The intracolumnar stacking distance for all the **HDBPs** is approx. 3.5 Å, smaller than the van der Waals sum of 3.54 Å,²³ and is in consistent with a good π -stacking tendency.

Much effort has been carried out for broadening the mesogenic range of single component discotic liquid crystals.²⁴⁻²⁸ The fact that **HDBP-1, 2, 3, 4** and **5** exhibit a low melting and a relatively high clearing temperature provide the

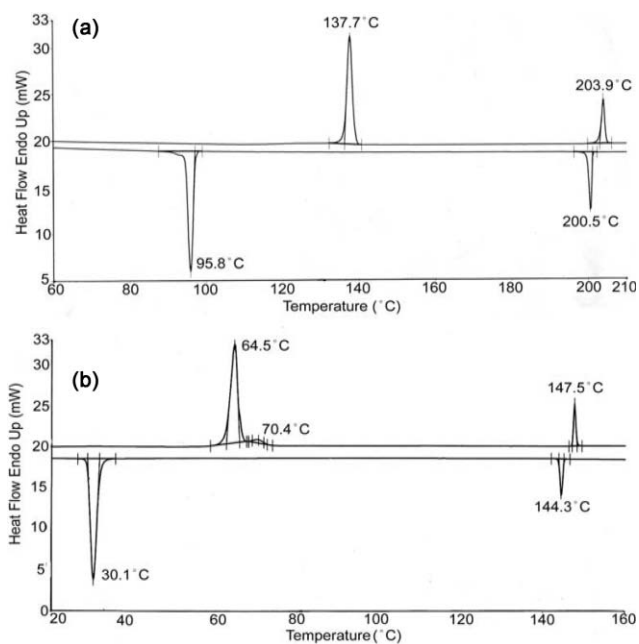


Fig. 2 DSC curves of (a) **HDBP-1** and (b) **HDBP-3**. The transition temperatures (°C) were determined by DSC at 10 °C min⁻¹.

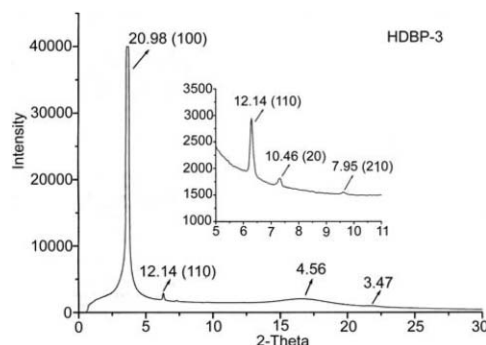


Fig. 3 Powder X-ray diffraction pattern of **HDBP-3** at 80 °C.

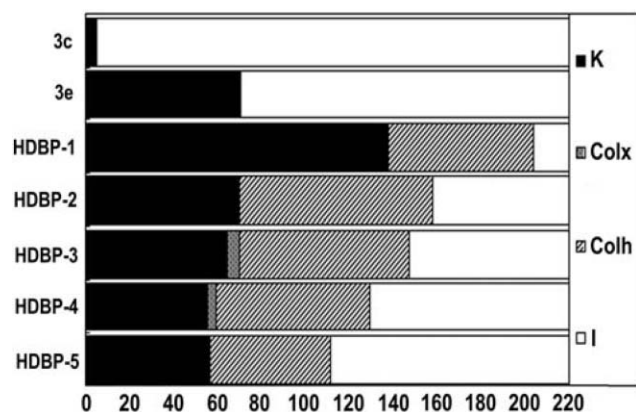


Fig. 4 Graphical representation of the phase ranges for **3c**, **3e** and **HDBP-1-5**.

basis for their relatively wide mesophase range of between 55–90 °C (Fig. 4), whereas the mesogenic range for triphenylenes with similar peripheral alkoxy chains is in the range of 10–30 °C.^{1,21} Whereas the synthesis of a triphenylene core with lateral dipole to improved mesophase range is tedious, our **HDBPs** with a build-in dipole can be readily synthesized.

Conclusions

In conclusion, hexaalkoxydibenzo[*a,c*]phenazines, **HDBP-1**, **2**, **3**, **4** and **5**, with long carbon chains have been shown to exhibit liquid crystalline behavior. We have highlighted the issue of incorporating dual effects arising as a result of using unsymmetrical-core, dipole-core and peripheral side chains to improve the mesogenic behavior of these discotic liquid crystals. These could lead to the synthesis of favorable discotic compounds which are more suitable for applications in electronic devices due to their lower crystal-to-mesophase transition temperature and broader mesophase temperature range. We are continuing to pursue the design of new hexaalkoxydibenzo[*a,c*]phenazines to optimize the LC properties.

Experimental

General

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware. Dichloromethane was distilled over calcium hydride. 1,2-bisalkoxy-4,5-diaminobenzene⁷ and tetraalkoxyphenanthrene-9,10-dione¹⁵⁻¹⁷ were prepared according to the published procedures. Nuclear magnetic resonance spectra were recorded on a Varian Gemini-200 MHz and Varian Unity-INOVA-500 MHz spectrometer. (CDCl₃). Chemical shifts are reported in ppm relative to residual CHCl₃ (δ = 7.26, ¹H; 77.0, ¹³C). Mass spectra were obtained on JEOL JMS-HX110 or ESI on Bruker APE (II) FT-MS and elemental analyses were carried out on a Heraeus CHN-O Rapid Elementary Analyzer.

Instrumental

Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris1 with heating and cooling rates of 5 and

10 °C min⁻¹. Polarized optical microscopy (POM) was carried out on a OLYMPUS CX41 with a Mettler FP90/FP82HT hot stage system. X-Ray powder diffraction data were collected on the wiggler beamline BL17A of the National Synchrotron Radiation Research Center (NSRRC), Taiwan, using a triangular bent Si(111) monochromator and a wavelength of 1.334431 Å. The sample in a 1 mm capillary was mounted on the Huber 5020 diffractometer. An air stream heater is equipped at BL17A beamline and the temperature controller is programmable by a PC with a PID feedback system.

Synthesis

General procedure for the preparation of **3c**, **3e** and hexaalkoxydibenzo[*a,c*]phenazines (**HDBPs**): to a solution of tetraalkoxybenzil **1** (0.01 mol) or tetraalkoxyphenanthrene-9,10-dione **4** (0.01 mol) and 1,2-bisalkoxy-4,5-diaminobenzene (0.01 mol) in dichloromethane (35 mL) was added acetic acid (3.0 mL). The reaction mixture was stirred under nitrogen for 1 day. Removal of the solvent give crude product that has to be purified.

The crude products were purified by column chromatography on silica gel using dichloromethane as eluent and this give some pure **3**, together with fractions containing mixtures of compounds. The mixtures were again column chromatographed several times. Compound **3**, obtained from chromatography, was re-crystallized from ethyl acetate or co-solvent (methanol–dichloromethane) at least five times to give pure **3** as a white solid.

The crude products from the preparation of **HDBPs** was column chromatography once on silica gel with dichloromethane as eluent to give yellowish solid. Pure **HDBPs** can be readily obtained by re-crystallization from ethyl acetate or hexane. Preparative TLC (EtOAc–hexane (1 : 5)) can also be used to obtain pure **HDBPs**.

The yield of **3c** is 35%, **3e** is 40% after purification. The yield of **HDBP-1** is 38%, **HDBP-2** is 35%, **HDBP-3** is 33%, **HDBP-4** is 34%, and **HDBP-5** is 32% from route B after purification to give a very pure sample.

3c: ¹H NMR (CDCl₃, 500 MHz): δ 7.41 (s, 2H), 7.07 (dd, 2H, *J* = 9.2 and 1.0 Hz), 7.01 (d, 2H, *J* = 1.0 Hz), 6.83 (d, 2H, *J* = 8.5 Hz), 4.18 (t, 4H, *J* = 6.5 Hz), 3.99 (t, 4H, *J* = 6.5 Hz), 3.81 (t, 4H, *J* = 6.5 Hz), 1.93 (quint, 4H, *J* = 7.0 Hz), 1.82 (quint, 4H, *J* = 7.0 Hz), 1.71 (quint, 4H, *J* = 7.0 Hz), 1.57–1.21 (m, 60H), 0.94–0.84 (m, 18H); ¹³C NMR (CDCl₃, 125 MHz): δ 152.54, 150.26, 149.35, 148.61, 137.83, 132.04, 122.56, 115.28, 113.24, 107.06, 69.15, 69.12, 69.05, 34.61, 31.81, 31.80, 31.77, 31.54, 29.38, 29.34, 29.29, 29.25, 29.22, 29.21, 29.11, 28.79, 26.11, 25.99, 25.22, 22.65, 22.62, 22.60, 14.04; LRMS (FAB): 1052 (*M*⁺ + 1, 29.07); anal. calcd for C₆₈H₁₁₀N₂O₆: C, 77.37; H, 10.54; N, 2.66. Found: C, 77.67; H, 10.48; N, 2.52%.

3e: ¹H NMR (CDCl₃, 500 MHz): δ 7.38 (s, 2H), 7.07 (dd, 2H, *J* = 8.5 and 2.0 Hz), 7.00 (d, 2H, *J* = 2.0 Hz), 6.82 (d, 2H, *J* = 8.5 Hz), 4.18 (t, 4H, *J* = 6.5 Hz), 3.99 (t, 4H, *J* = 6.5 Hz), 3.81 (t, 4H, *J* = 6.5 Hz), 1.93 (quint, 4H, *J* = 7.0 Hz), 1.82 (quint, 4H, *J* = 7.0 Hz), 1.71 (quint, 4H, *J* = 7.0 Hz), 1.56–1.21 (m, 108H), 0.93–0.85 (m, 18H); ¹³C NMR (CDCl₃, 125 MHz): δ 152.43, 150.44, 149.29, 148.63, 137.98, 132.36, 122.53, 115.29, 113.30, 107.25, 69.20, 69.12, 69.07, 31.92, 31.84,

31.82, 31.77, 31.54, 29.68, 29.65, 29.61, 29.40, 29.38, 29.36, 29.32, 29.28, 29.24, 29.14, 28.83, 26.01, 22.68, 22.65, 22.62, 22.60, 14.11, 14.09; LRMS (FAB): 1388 (M^+ , 18.11); anal. calcd for $C_{92}H_{158}N_2O_6$: C, 79.60; H, 11.47; N, 2.02. Found: C, 79.67; H, 11.40; N, 2.05%.

HDBP-1: 1H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 2H), 7.76 (s, 2H), 7.56 (s, 2H), 4.36 (t, J = 6 Hz, 8H), 4.28 (t, J = 6.5 Hz, 4H), 2.01–1.93 (m, 12H), 1.64–1.58 (m, 12H), 1.08–1.05 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.85, 151.06, 149.38, 139.31, 138.95, 125.71, 123.99, 108.03, 106.63, 106.44, 69.32, 68.87, 68.81, 31.39, 30.97, 19.39, 19.33, 13.98, 13.91; MALDI-TOF: 731; HRMS (ESI) m/z 713.4525 (713.4529 calculated for $C_{44}H_{61}N_2O_6$ [$M + H^+$]).

HDBP-2: 1H NMR ($CDCl_3$, 500 MHz): δ 8.79 (s, 2H), 7.76 (s, 2H), 7.60 (s, 2H), 4.36 (t, J = 6.5 Hz, 4H), 4.30–4.26 (m, 8H), 2.02–1.94 (m, 12H), 1.64–1.36 (m, 36H), 0.96–0.93 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.99, 151.17, 149.42, 125.79, 108.05, 106.43, 69.64, 69.21, 69.15, 31.66, 31.57, 29.34, 29.28, 28.89, 25.84, 25.81, 25.76, 22.65, 22.61, 14.07, 14.04, 140.02; MALDI-TOF: 880; HRMS (ESI) m/z 881.6410 (881.6407 calculated for $C_{56}H_{85}N_2O_6$ [$M + H^+$]).

HDBP-3: 1H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 2H), 7.77 (s, 2H), 7.53 (s, 2H), 4.35 (t, 4H, J = 6.5 Hz), 4.27 (t, 8H, J = 6.5 Hz), 2.04–1.92 (m, 12H), 1.64–1.54 (m, 12H), 1.48–1.28 (m, 48H), 0.92–0.88 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.75, 150.99, 149.35, 139.45, 139.11, 125.68, 124.18, 107.99, 106.74, 106.50, 69.66, 69.12, 69.07, 31.853, 31.846, 31.83, 29.48, 29.46, 29.41, 29.37, 29.35, 29.33, 29.28, 28.95, 26.18, 26.16, 26.09, 22.69, 14.11; LRMS (FAB): 1049 (M^+ , 19.98); anal. calcd for $C_{68}H_{108}N_2O_6$: C, 77.81; H, 10.37; N, 2.67. Found: C, 77.68; H, 10.38; N, 2.65%.

HDBP-4: 1H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 2H), 7.76 (s, 2H), 7.54 (s, 2H), 4.35 (t, J = 6.5 Hz, 8H), 4.27 (t, 8H, J = 6.5 Hz), 2.02–1.94 (m, 12H), 1.62–1.28 (m, 84H), 0.91–0.87 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.78, 151.00, 149.35, 139.40, 139.06, 125.69, 124.13, 108.01, 106.71, 106.51, 69.67, 69.13, 69.08, 31.93, 29.68, 29.63, 29.62, 29.59, 29.54, 29.50, 29.42, 29.38, 29.36, 28.95, 26.18, 26.16, 26.09, 22.69, 14.11; MALDI-TOF: 1217; HRMS (ESI) m/z 1218.0079 (1218.0085 calculated for $C_{80}H_{133}N_2O_6$ [$M + H^+$]).

HDBP-5: 1H NMR ($CDCl_3$, 500 MHz): δ 8.76 (s, 2H), 7.76 (s, 2H), 7.53 (s, 2H), 4.35 (t, 4H, J = 6.5 Hz), 4.27 (t, 8H, J = 6 Hz), 2.04–1.90 (m, 12H), 1.66–1.52 (m, 12H), 1.49–1.20 (m, 96H), 0.98–0.84 (m, 18H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.74, 150.97, 149.34, 139.45, 139.12, 125.67, 124.20, 107.99, 106.75, 106.50, 69.67, 69.11, 69.05, 31.93, 31.58, 29.74, 29.68, 29.63, 29.54, 29.51, 29.42, 29.38, 28.97, 28.90, 26.17, 26.11, 25.77, 22.69, 22.62, 14.11, 14.04; LRMS (FAB): 1385 (M^+ , 7.12); anal. calcd for $C_{92}H_{156}N_2O_6$: C, 79.71; H, 11.34; N, 2.02. Found: C, 79.52; H, 11.43; N, 1.95%.

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