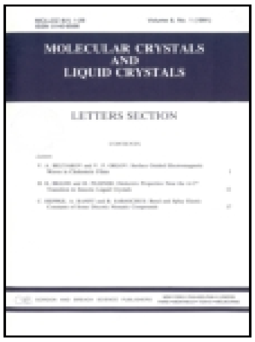

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Sodium Ion Complexation Enforced Columnar Mesophase of Dibenzo[*a*,*c*]phenazine Bearing Lateral Crown Ether

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The dibenzo[a,c]phenazine discogen having "π-polarization" containing a lateral crown ether and four alkoxy-peripheral side chain, ***DBPZ-C$_n$*** *were synthesized. These metal-free crown ether* ***DBPZ-C$_n$*** *having four dodecylalkoxy side chains were found to be non-mesogenic. The columnar mesophase can be augmented by complexation of the crown ether moiety with sodium ion for* ***DBPZ-C$_{12}$-Na****. XRD investigation revealed the formation of rectangular columnar mesophase for* ***DBPZ-C$_{12}$-Na****.*

Keywords dibenzo[*a,c*]phenazine-crown ether; dipole; sodium complex; enforced packing

Introduction

Unique interaction of crown structure makes themselves attractive in supermolecular chemistry and material science. The application of crown ether molecules has been extended into many aspects, such as chemo-sensor [1], molecular recognition [2, 3], membrane [4], and liquid crystal materials [5, 6]. Since 1980, mesomorphic crown ethers have started to be widely investigated. For crown-ether containing liquid crystals, crown ether can be positioned at the lateral or central position with respect to the mesogen which can be of different shape, such as, rod, disc, polycatenar, tape-shaped, dendrimer or polymer [5–8]. Moreover, the cavity size of crown ether determines which type of cations for complexation. The most studied in the context of liquid crystal is the benzo-15-crown-5, whereby sodium cation can perfectly fit into the crown ether's cavit [7]. This is because that the size of benzo-15-crown-5 is 1.7–2.2 Å and the cationic diameter of NaI is 1.94 Å. Laschat and co-workers have, has synthesized ortho-terphenyl units bearing both lateral and central benzo-15-crown-5 liquid crystals with and without metal complexation [9–12]. In general, cation complexation with alkaline metal induced new mesophases such as from nematic or smetic to columnar phase; and at the same time stabilized the mesophase further. In contrast, He and coworkers reported a mesophase destabilization upon cation complexation for calamitic liquid crystals bering lateral crown ether [13]. The comparison of the mesomorphic properties of mesogens with different side chain on

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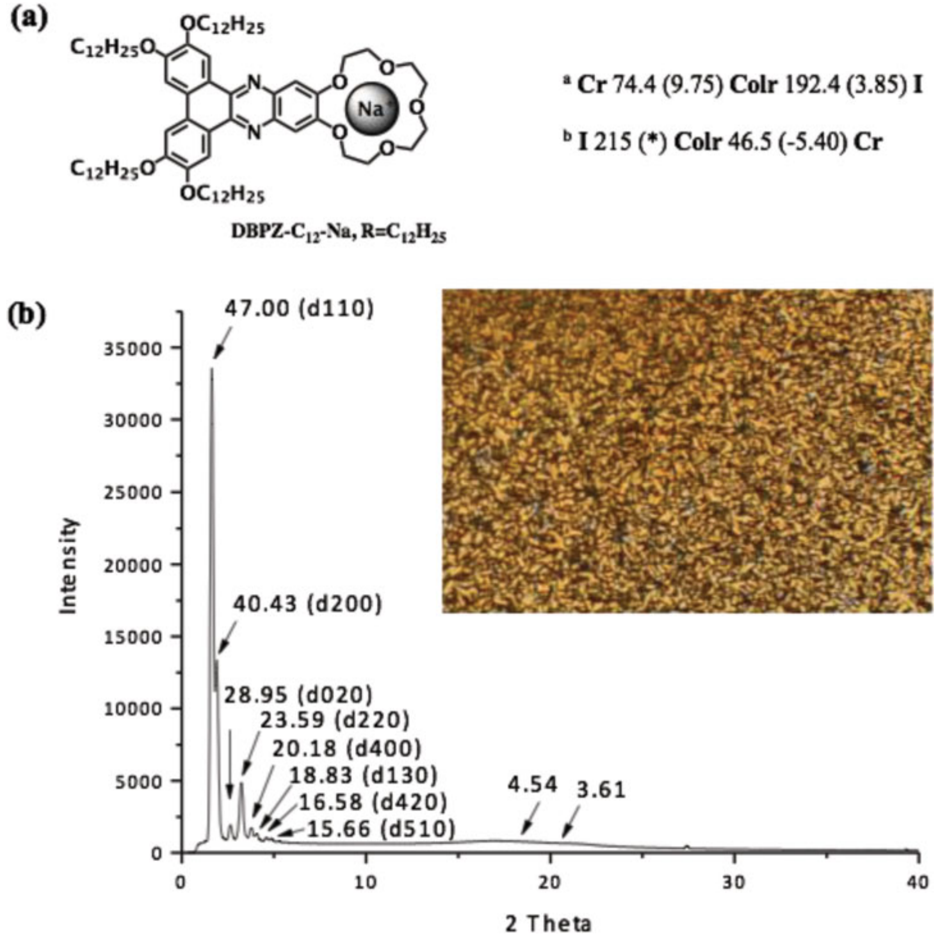


Figure 1. (a) The molecular structure of **DBPZ-C$_{12}$-Na** and the phase transition temperatures and associated enthalpies (kJ/mol^{-1}) for second heating, (b) microscropy texture at 160°C on cooling, and X-ray diffraction on second heating, at 110°C.

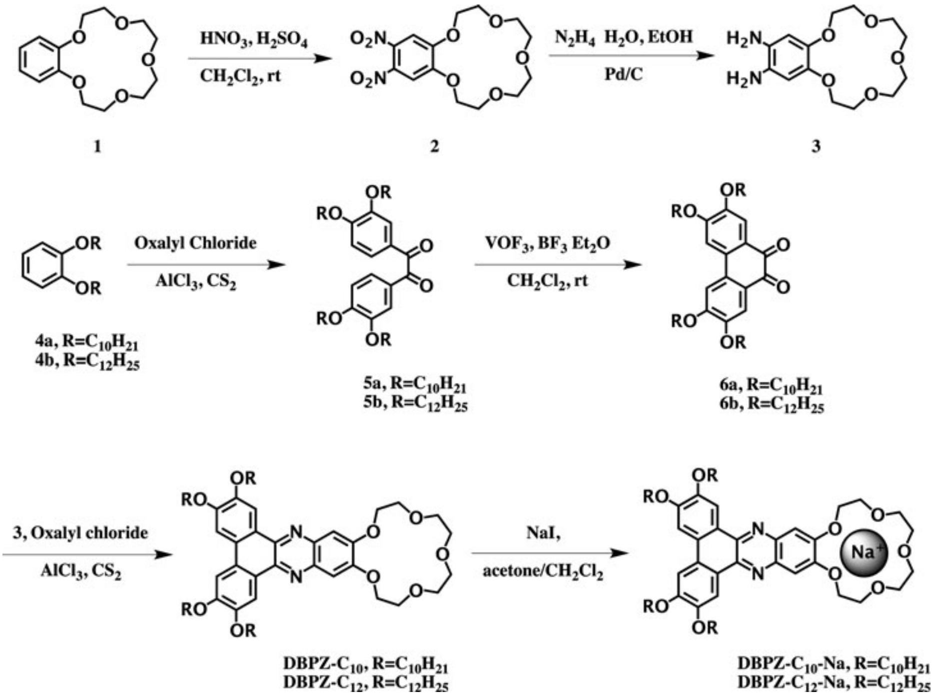
ortho-tetraphenyl units and some alkaline salt has been studied. [10–12]. Nevertheless, the influence of a more geometrically constrain core and core polarity on the structure-property relationship of crown ether bearing thermotropic liquid crystal has not been studied.

Dibenzo[*a,c*]phenazine, which contains a π-polarized disc possesses a dipole moment along the longer molecular axis, is a well studied mesogenic core for columnar liquid crystals synthesized by Williams et al and our laboratory. [14–17]. It will be of interest to study the influence of the larger fused core of dibenzo[*a,c*]phenazine with polarity at the core bearing lateral 15-crown ether and the sodium ion complexation on the mesomorphic properties. With this in mind, 2,3,6,7-tetrakis(dodecyloxy)-12,13,15,16,18,19,21,22-octahydro-dibenzo[*a,c*][1,4,7,10,13]-pentaoxacyclopentadeca[2,3-i]-phenazine compound, **DBPZ-C$_n$** were synthesized. The new compounds were characterized unambiguously by ^{1}H and ^{13}C NMR spectroscopy and MALDI-TOF mass spectrometry.

Hence, mesomorphic crown ethers have been synthesized, and their mesomorphic properties were investigated.

Results and Discussion

The crown ether compounds **DBPZ-C_n** were synthesized by the condensation of 2,3,6,7-tetrakis(alkoxy)phenanthrene-9,10-dione **6** [17], and diamino-crown compound **3** [18], under acid catalysis in CH_2Cl_2, and purified rigorously by aluminium oxide (Activity V) column chromatography (Scheme 1). The diamino-crownm benzene **3** was derived from reduction with palladium on charcoal in the presence of hydrazine monohydrate and used *in situ*. The purification process is tedious and needs to be repeated several times in order to obtain highly pure compound **DBPZ-C_n**, suitable for determining the liquid crystal properties. Furthermore, the sodium ion complex was prepared by dissolving **DBPZ-C_n** and sodium iodide in dichloromethane/acetone solution, standing for 18 hours, and the solvent was then evaporated at ambient temperature. The complex **DBPZ-C_n-Na** was dried under high vacuum.



Scheme 1. The synthesis routs of compound **DBPZ-C_x** and corresponding metal salts **DBPZ-C_x-Na**.

The mesogenic behavior was further studied by polarized optical microscopy (POM), differential scanning calorimetry (DSC) and variable temperature X-ray diffraction (XRD). The DSC results, together with POM for **DBPZ-C_{10}** and **DBPZ-C_{12}** revealed only isotropic melting from the crystalline state at around100°C. This is in contrast to the tetradodecyloxy side chain of ortho-terphenyl lateral crown that exhibit liquid crystalline properties. [9] Thus the introduction of a more rigid, larger aromatic core, and having a dipole along the core, was found to prevent mesophase formation. We emphasize that there is no preference of the two opposite forces for packing, the microphase separation between immiscible crown and paraffinic side chains and the preferred dipole cancellation of the core within the column through anti-parallel packing, for both **DBPZ-C_{10}** and **DBPZ-C_{12}**. This leads to random packing without the ability to form liquid crystalline phases.

Unexpectedly, the sodium complex, **DBPZ-C_{10}-Na** is also not liquid crystalline. To our delight, **DBPZ-C_{12}-Na** show liquid-crystalline behavior as deduced from the DSC and POM. The crystalline melts into mesophase at 74.4°C and then enters into isotropic phase at 192.4°C on second heating (Figure 1a). The mesophase range is very large for **DBPZ-C_{12}-Na**. On cooling, liquid crystalline texture was observed with small domain under the POM (Figure 1b). The corresponding X-ray diffraction taken at heating 160°C confirmed the formation of columnar phase with *C2mm* symmetry, a = 77.80 Å, b = 54.12 Å (Figure 1b), this being rectangular. Similar XRD diffraction was observed at 110°C. The complexation of the crown ether in **DBPZ-C_{12}-Na** has led to the formation of supramolecular assembly in the liquid crystalline phase.

Conclusion

A new series of dibenzo-[*a,c*]phenazine discogen bearing 15-crown-5-ether has been prepared and their mesomorphic properties studied. The metal-free crown ether-based dibenzo[*a,c*]phenazine material was non-mesomorphic; however, complexation with sodium metal (NaI), as for **DBPZ-C_{12}-Na**, showed rectangular columnar mesophase with *C2mm* symmetry. There is a striking difference in properties for using dibenzo[*a,c*]phenazine, which possesses a dipole moment along the longer molecular axis which give wide mesogenic temperature range (approx. 120°C). The forces driving the packing have not been fully understood and future on-going work will attempt to rationalize the factors involved, together with studying the influence of alkali salts on mesomorphic properties.

Experimental

All reactions were conducted under an atmosphere of nitrogen in oven-dried glassware. Dichloromethane was distilled over calcium hydride. Nuclear magnetic resonance spectra were recorded on a Varian Unity-INOVA-500 MHz spectrometer using $CDCl_3$ as solvent. Chemical shifts are reported in ppm relative to residual $CDCl_3$ ($\delta = 7.26$, ^1H, 77.0, ^{13}C). Mass spectra were obtained on FT-MS on Bruker APEX II or MALDI-TOF on Bruker Autoflex III TOF/TOF. Elemental analyses were carried out on Heraeus CHN-O Rapid Elementary Analyzer and Elementar vario EL □. Differential scanning calorimetry (DSC) was measured on a Perkin-Elmer Pyris 1 with heating and cooling rates of 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 (XRD) 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 1.333621 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.

Compound **3**[18] and **6**[17] were prepared according to reported procedures.

2,3,6,7-tetrakis(dodecyloxy)-12,13,15,16,18,19,21,22-octahydrodibenzo[a,c]-[1, 4, 7,-10,13]pentaoxacyclopentadeca[2,3-i]phenazine **DBPZ-C$_{12}$**. To a round-bottom flask containing 2:1 molar ratio of diketone **6** and diamine **3** were dissolved in anhydrous dichloromethane. Catalytical amount of acetic acid (1 mL) was added and the mixture was stirred for 18 hours. Removal of the solvent by rotary evaporator gave crude product that has to be rigorously purified by column chromatography of silica/Al_2O_3 (V) mixture, using dichloromethane as the eluent. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.74 (s, 2H), 7.76 (s, 2H), 7.49 (s, 2H), 4.38~4.37 (m, 4H), 4.33 (t, $J = 6.5$ Hz, 4H), 4.27 (t, $J = 6.5$ Hz, 4H), 4.04~4.03 (m, 4H), 3.85~3.82 (m, 8H), 1.99~1.95 (m, 8H), 1.75~1.22 (m, 72 H), 0.89~0.87 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.37, 151.05, 149.33, 139.57, 139.10, 125.74, 124.08, 107.99, 106.85, 106.46, 71.27, 70.12, 69.63, 69.05, 68.36, 31.92, 29.72, 29.69, 29.67, 29.53, 29.50, 29.40, 29.37, 29.35, 26.17, 26.16, 22.67, 14.10. MALDI-TOF: 1208.206 [M+H$^+$]; Anal. Calcd for: $C_{76}H_{122}N_2O_9$: C, 75.58; H, 10.18; N, 2.32. Found: C, 75.30; H, 10.25; N, 2.18.

2,3,6,7-tetrakis(decyloxy)-12,13,15,16,18,19,21,22-octahydrodibenzo[a,c]-[1,4,7,-10,13]pentaoxacyclopentadeca[2,3-i]phenazine **DBPZ-C$_{10}$**. **DBPZ-C$_{10}$** was prepared according to a similar procedure to **DBPZ-C$_{12}$**. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.74 (s, 2H), 7.76 (s, 2H), 7.50 (s, 2H), 4.38 (d, $J = 4.0$ Hz, 4H), 4.34 (t, $J = 6.5$ Hz, 4H), 4.27 (t, $J = 6.5$ Hz, 4H), 4.04 (s, 4H), 3.86~3.82 (m, 8H), 1.99~1.95 (m, 8H), 1.70~1.25 (m, 56 H), 0.90~0.87 (m, 12H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.38, 151.06, 149.35, 139.60, 139.10, 125.76, 124.08, 107.99, 106.88, 106.48, 71.25, 70.11, 69.65, 69.05, 68.36, 31.92, 29.68, 29.61, 29.53, 29.49, 29.40, 29.37, 29.35, 26.17, 26.16, 22.68, 14.10. MALDI-TOF: 1096.112 [M+H$^+$]; Anal. Calcd for: $C_{68}H_{106}N_2O_9$: C, 78.68; H, 9.40; N, 5.56.

Preparation of the complex: Complex of **NaI-CM-1** with sodium iodide was performed in the mixture solvent (dry dichloromethane/acetone solution) for 18 hours. Evaporation of the solvent at room temperature was under reduced pressure and subsequently dried under vaccum.

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