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## Self-assembled 1,2-bis[4-(4-(10-decyloxy)phenylazo)]benzoylhydrazine dimer and its hydrogen-bonded complexes

Guan-Yeow Yeap<sup>a\*</sup>, Subramanian Balamurugan<sup>a</sup>, Samikannu Rakesh<sup>b</sup>, Chun-Chieh Han<sup>c</sup> and Hong-Cheu Lin<sup>c</sup>

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We report the synthesis and investigation of a new self-assembled benzoylhydrazine-based compound, namely 1,2-bis[4-(4-(10-decyloxy)phenylazo)]benzoylhydrazine and their hydrogen-bonded complexes with different carboxylic acid derivatives, of which some exhibit liquid crystalline properties and some are non-mesogens. The conversion of the non-liquid crystalline target compound that is free from carboxylic acid to liquid crystalline complexes containing various carboxylic acids can probably be rationalised through the breaking of intermolecular hydrogen bonding within the supramolecular assembly by carboxylic acid dopants. The enhancement of liquid crystalline properties of benzoylhydrazine compounds with respect to various carboxylic dopants is documented. Other salient features can be exemplified by the formation of discotic columnar phase as shown by the azo-linkage containing 4-(4'-(10-decyloxy)phenylazo)benzoic acid-doped complex.

**Keywords:** liquid crystalline; hydrogen bonding; supramolecular assembly; discotic columnar phase

### 1. Introduction

The supramolecular assembly plays an important role in the design and engineering of architectures of chemical molecules (1, 2). Although the conventional chemical structures involve the covalent bond, supramolecular chemistry places emphasis on the weaker non-covalent interactions between molecules. These forces include hydrogen bonding (H-bonding), van der Waals force, dative bonds associated with coordination compounds, hydrophobic force and electrostatic effect. Among these, the H-bonding can alter the liquid crystalline properties through rigidity and molecular order (3). The importance of H-bonding towards the formation and/or stabilisation of liquid crystalline phases has actually received growing attention in recent years (4–6). The same phenomenon can also be observed in the typical liquid crystal dimers of aromatic carboxylic acids (7) and their analogue possessing supramolecular assembly (8); polymeric assembly of plural molecules (9); assembly of molecules in the side-chain polymers (10) and formation of bent shape, hockey-stick shape, disc shape and star shape molecules (11–13). Some of the related reports described the presence of intermolecular H-bonding at the end of the mesogen as a prerequisite to command a specific molecular shape (14, 15). However, the intermolecular H-bonding introduced at the middle of the mesogen seemed to enhance the molecular order.

In this paper, we report the synthesis of difunctional (donor and acceptor) benzoylhydrazine-containing compounds with alkyl chain (C<sub>10</sub>H<sub>21</sub>–) at both ends of terminals.

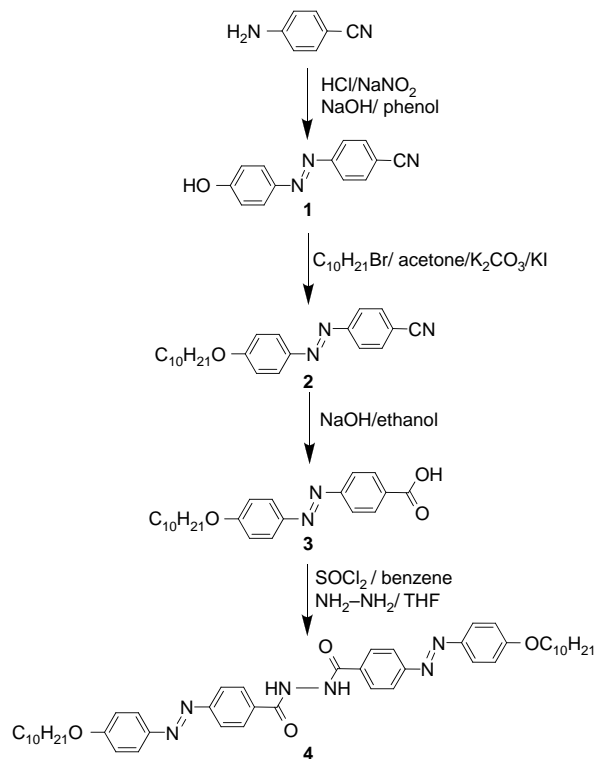
Since the target compound inherently possesses donor (–NH) and acceptor (–C=O) between the two mesogenic units, it induces the polymeric self-assembly through intermolecular hydrogen bonding. However, the use of carboxylic acid (non-liquid crystalline and liquid crystalline) to break down the polymeric self-assemblies as a way to convert the non-liquid crystalline benzoylhydrazines to mesogenic complexes will also be reported in the present report.

### 2. Experimental

#### 2.1. Materials and methods

The chemicals were obtained from Sigma-Aldrich Chemicals (St. Louis, Missouri, USA) and Merck (Darmstadt, Germany). All the solvents were purified and dried by standard methods, and the crude samples were purified by column chromatographic technique using silica gel (230–400 mesh) as a stationary phase. Thin-layer chromatography was performed on aluminium sheets pre-coated with silica gel (Merck, Kieselgel 60, F254). The infrared (IR) spectra for all compounds were recorded in the range 4000–400 cm<sup>–1</sup> using a PerkinElmer 2000 FT-IR spectrophotometer (Waltham, Massachusetts, USA) with the samples embedded in KBr discs. The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were obtained using a Bruker 500 MHz Ultra-Shield spectrometer (Karlsruhe, Germany). CDCl<sub>3</sub> and DMSO-*d*<sub>6</sub> were used as solvents and trimethylsilane as the internal standard. Carbon, Hydrogen and Nitrogen microanalyses were carried out on a PerkinElmer 2400 LS Series CHNS/O

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Scheme 1. Synthetic pathway towards the formation of compound 4.

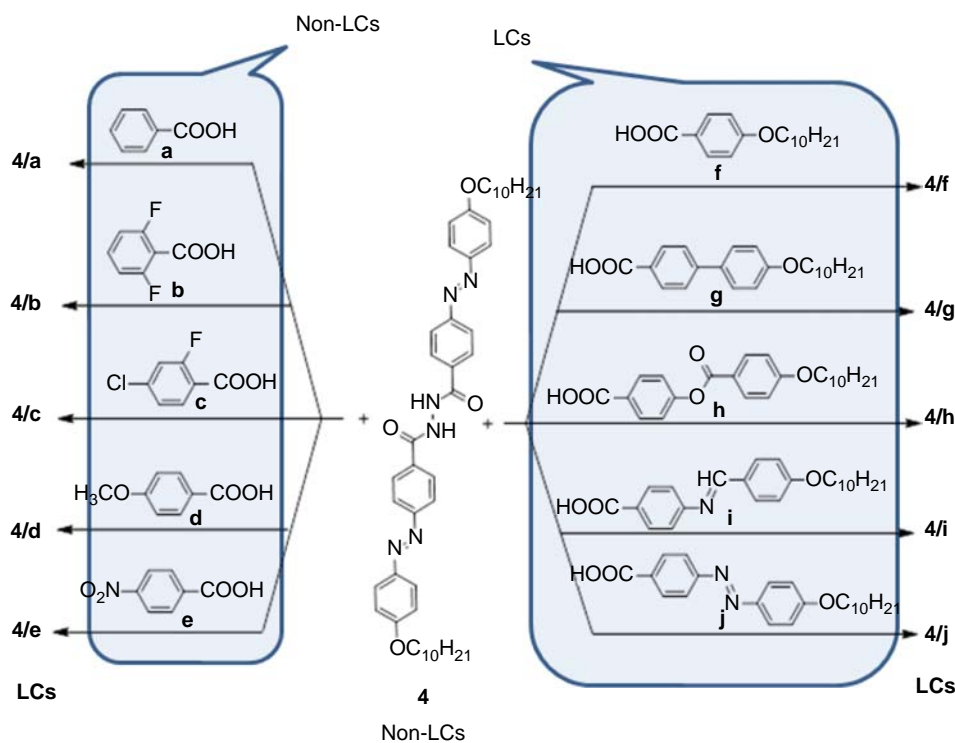
Analyzer (Waltham, Massachusetts, USA). The liquid crystalline textures were observed under a Carl Zeiss Axioskop 40 polarising microscope (Oberkochen, Germany) equipped with a Linkam TMS94 temperature controller (Guildford, Surrey, UK) and a LTS350 hot stage (Guildford, Surrey, UK). The transition temperatures and enthalpy changes were measured by a differential scanning calorimeter TA Q200 (Delaware, New Castle, USA) at a rate of  $5^{\circ}\text{C min}^{-1}$  for both heating and cooling cycles.

## 2.2. Synthesis

The synthetic methods used to obtain all intermediates 1–3, compound 4 (Scheme 1) and hydrogen-bonded complexes (Scheme 2) are described.

### 2.2.1. Synthesis of 4-(4'-(10-dodecyloxy)phenylazo)benzonitrile (1)

4-Cyanoaniline (0.07 mol) was dissolved in a mixture of hydrochloric acid (16 ml) and water (16 ml), and the reaction mixture was cooled in ice bath with constant stirring at  $0-5^{\circ}\text{C}$ . A solution of sodium nitrite (0.07 mol) in 20 mL of water was added dropwise to the reaction mixture. Phenol (0.07 mol) was dissolved in 10% sodium hydroxide solution (45 ml) in a round-bottomed flask, and the solution was cooled to  $5^{\circ}\text{C}$ . The reaction mixture was



Scheme 2. Synthetic pathway for the formation of complexes 4a–4j.

vigorously stirred and cold diazonium salt solution was added dropwise, and then the mixture was kept in an ice bath for 30 min. Upon completion of the reaction, the mixture was poured into water (500 ml) and acidified with aqueous hydrochloric acid to get an orange colour product. The crude product was filtered through a Buchner funnel (Shanghai Gongtao Ceramics Co., Ltd., Shanghai, China) with gentle suction and washed well with water. The resulting product was an orange-red colour solid and dried in vacuum oven at 60°C for 24 h (yield: 66%).

*Elemental analysis.* Calcd for  $C_{13}H_9N_3O$ : C, 69.95; H, 4.06; N, 18.82, found: C, 69.90; H, 4.00; N, 18.75. FT-IR (KBr pellet)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3319 (—OH), 2235(—CN), 1582 (—C=C—), 1421 (—N=N—).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 7.92 (d, 2H,  $J = 8.4$  Hz, ArH), 7.73 (d, 2H,  $J = 8.8$  Hz ArH), 7.19 (d, 2H,  $J = 8.8$  Hz, ArH), 6.98 (d, 2H,  $J = 8.2$  Hz, ArH).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 159.5, 154.7, 146.9, 133.1, 125.6, 123.1, 118.1, 116.0, 113.2.

### 2.2.2. Synthesis of 4-(4'-(10-decyloxy)phenylazo)benzonitrile (2a)

The compound 4-(4'-(10-decyloxy)phenylazo)benzonitrile was synthesised by suspension of 4-(4'-hydroxyphenylazo)benzonitrile (0.01 mol), anhydrous  $\text{K}_2\text{CO}_3$  (0.02 mol) and a pinch of potassium iodide (KI) in dry dimethylformamide (DMF) (80 ml). 1-Bromodecane (0.01 mol) was added dropwise to the reaction mixture and refluxed at 90°C for 24 h. Upon completion of the reaction, the mixture was filtered and washed with excess of DMF. The filtrate was poured into ice water, extracted using diethyl ether and dried with anhydrous sodium sulphate. The solvent was evaporated under reduced pressure and purified by column chromatography over silica gel using chloroform as an eluent. Thus, an orange-coloured solid was obtained with 75% yield.

*Elemental analysis.* Calcd for  $C_{22}H_{27}N_3O$ : C, 75.61; H, 7.79; N, 12.02, found: C, 75.58; H, 7.81; N, 12.11. FT-IR (KBr pellet)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3011 (—CH<sub>3</sub>), 2921, 2848 (—CH<sub>2</sub>—), 2233 (—CN), 1648, 1475 (—C=C—) aromatic, 1421 (—N=N—), 1252, 1111 (—OCH<sub>2</sub>—).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.42 (d, 2H,  $J = 8.5$  Hz, ArH), 7.88 (d, 4H,  $J = 9.9$  Hz, ArH), 7.21 (d, 2H,  $J = 8.6$  Hz, ArH), 4.56 (t, 2H,  $J = 7.2$  Hz, —OCH<sub>2</sub>), 1.72 (q, 2H, —CH<sub>2</sub>), 1.81 (q, 2H, —CH<sub>2</sub>), 1.64 (m, 2H, —CH<sub>2</sub>), 1.56 (m, 2H, —CH<sub>2</sub>), 1.41 (m, 2H, —CH<sub>2</sub>), 1.37 (m, 2H, —CH<sub>2</sub>), 0.95 (t, 3H,  $J = 7.6$  Hz, —CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 161.7, 155.1, 146.1, 133.6, 122.2, 117.1, 114.0, 113.1, 67.8, 32.1, 29.1, 28.3, 25.1, 19.4, 14.0.

### 2.2.3. Synthesis of 4-(4'-(10-decyloxy)phenylazo)benzoic acid (3a)

A mixture of 4-(4'-(7-decyloxy)phenylazo)benzonitrile (0.05 mol), potassium hydroxide (0.1 mol) and ethanol

(100 ml) was refluxed for 4 h. The reaction mixture was poured into water (500 ml) and acidified with aqueous hydrochloric acid. The crude product was filtered off and washed with water and recrystallised from ethanol (yield: 95%).

*Elemental analysis.* Calcd for  $C_{22}H_{28}N_2O_3$ : C, 71.71; H, 7.66; N, 7.90, found: C, 71.51; H, 7.29; N, 7.81. FT-IR (KBr pellet)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3409 (—OH), 3015 (—CH<sub>3</sub>), 2919, 2854 (—CH<sub>2</sub>—), 1706 (acid-C=O), 1475 (—C=C—) aromatic, 1421 (—N=N—), 1252, 1178 (—OCH<sub>2</sub>—).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 8.09 (d, 2H,  $J = 8.5$  Hz, ArH), 7.82 (d, 4H,  $J = 9.9$  Hz, ArH), 7.01 (d, 2H,  $J = 8.4$  Hz, ArH), 4.12 (t, 2H,  $J = 7.2$  Hz, —OCH<sub>2</sub>), 1.71–1.79 (q, 2H, —CH<sub>2</sub>), 1.43–1.48 (q, 2H, —CH<sub>2</sub>), 1.31–1.33 (m, 4H, —CH<sub>2</sub>), 0.91 (t, 3H,  $J = 7.6$  Hz, —CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  (ppm): 168.4, 162.6, 154.4, 146.2, 136.1, 132.7, 123.4, 121.9, 116.8, 115.6, 113.4, 68.2, 32.1, 29.2, 28.6, 25.6, 22.5, 13.4.

### 2.2.4. Synthesis of 1,2 bis4-(4-(10-decyloxy)phenylazo)benzoylhydrazine (4)

4-(4'-(10-Decyloxy)phenylazo)benzoic acid (3.8 g, 0.01 mol) was dissolved in benzene (50 ml) in the presence of one drop of dimethylformamide before thionyl chloride (1 ml; 0.015 mol) was added dropwise to the reaction mixture. The mixture was refluxed for 2 h with constant stirring. The benzene and excess thionyl chloride were removed under vacuum whereupon 4-(4'-(10-decyloxy)phenylazo)benzoylchloride was formed. It was dissolved in 100 ml dry tetrahydrofuran (THF) and added to the solution of hydrazine hydride (0.25 ml, 0.005 mol) in THF. Dry triethylamine (1.7 ml, 0.012 mol) was added and the reaction was carried out for 12 h. The precipitated triethylamine hydrochloride was removed by filtration and the precipitate was washed with THF. The filtrate was evaporated under reduced pressure and purified by column chromatography over silica gel using a mixture of ethylacetate–hexane (1:5) as an eluent that afforded the red-coloured solid (yield 87%).

*Elemental analysis.* Calcd for  $C_{46}H_{60}N_6O_4$ : C, 72.60; H, 7.95; N, 11.04, found: C, 72.58; H, 7.92; N, 11.53. FT-IR (KBr pellet)  $\nu_{\max}$  ( $\text{cm}^{-1}$ ): 3439 (—NH), 2915, 2849(—CH<sub>2</sub>—), 1600 (—C=O), 1497(—C=C—) aromatic, 1415 (—N=N—), 1197 (—OCH<sub>2</sub>—).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 10.52 (s, 1H, —NH), 10.34 (s, 1H, —NH), 7.94–7.98 (m, 8H,  $J = 9.8$  Hz, ArH), 7.79 (d, 4H,  $J = 8.5$  Hz, ArH), 7.02 (d, 4H,  $J = 8.0$  Hz, ArH), 4.05 (t, 4H,  $J = 6.8$  Hz, —OCH<sub>2</sub>), 1.81–1.84 (q,  $J = 7.6$  Hz, 4H, —CH<sub>2</sub>), 1.28–1.38 (m, 28H, —CH<sub>2</sub>), 0.88 (t, 6H,  $J = 7.6$  Hz, —CH<sub>3</sub>).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ),  $\delta$  (ppm): 162.8, 154.8, 146.7, 133.4, 128.0, 125.4, 125.2, 123.0, 122.8, 118.6, 114.8, 113.9, 113.1, 68.5, 31.8, 29.5, 29.3, 29.1, 26.0, 22.6, 14.0.

### 2.3. Preparation of hydrogen-bonded complexes

All hydrogen-bonded complexes were prepared by dissolution method. The compound **4** reacted with carboxylic acid in a molar ratio of 1:2 in the presence of distilled pyridine. The solution was stirred for 3 h at room temperature and the pyridine was allowed to slow evaporation, and the resulting solid was dried in vacuum for 24 h.

### 3. Results and discussion

Benzoylhydrazine-based azobenzene compound **4** was first synthesised and was subsequently used to form two series of hydrogen-bonded complexes. The first series consist of non-liquid crystalline compound **4** complexed with non-liquid crystalline carboxylic acid derivatives such as benzoic acid (**a**), 2,6-difluorobenzoic acid (**b**), 4-chloro-2-fluorobenzoic acid (**c**), 4-methoxyphenylacetic acid (**d**) and 4-nitrobenzoic acid (**e**). However, the second series consists of a non-liquid crystalline compound **4** complexed with liquid crystalline carboxylic acid derivatives such as 4-decyloxybenzoic acid (**f**), 4'-(decyloxy)biphenyl-4-carboxylic acid (**g**), 4-(4-(decyloxy)benzoyloxy)benzoic acid (**h**), 4-(4-(decyloxy)benzylideneamino)benzoic acid (**i**) and 4-(4'-(10-decyloxy)phenylazo)benzoic acid (**j**).

The FT-IR spectra of compound **4** and its complexes **4a–4j** were recorded and analysed. Figure 1 shows the comparison of the FT-IR spectra of benzoic acid, compound **4** and its complex **4a**. The benzoic acid prefers to form an acid dimer that exhibits a broad O–H absorption band at 2200–3400  $\text{cm}^{-1}$  and the C=O stretching band at 1686  $\text{cm}^{-1}$ . However, the FT-IR spectrum for the hydrogen-bonded complex **4a** showed the disappearance of the broad band at 2200–3400  $\text{cm}^{-1}$ , suggesting the absence of dimerisation of carboxylic acid (O–H $\cdots$ O=C) in the complexes. This observation indicates the formation of intermolecular H-bonding between the compound **4** and benzoic acid. The absorption bands of C=O group in the respective compound **4** and benzoic acid can be observed at 1600 and 1686  $\text{cm}^{-1}$ . The C=O absorption frequency for compound **4a** is found to be identical with that observed in benzoic acid. This can probably be attributed to the presence of identical hydrogen bonding within the respective benzoic acid and compound **4a**. Figure 2 illustrates the intramolecular H-bonding of these molecules which resemble the dimerisation of carboxylic acid (14). On the other hand, the absorption band ascribed to N–H stretching vibration is shifted from 3445 to 3439  $\text{cm}^{-1}$ , suggesting the formation of the hydrogen bond between N–H and O=C groups.

The phase sequence, transition temperatures and the associated enthalpies of the compound **4** and its complexes are summarised in Table 1. The compound **4** has a sharp melting point at 104.7°C. The absence of mesophase in

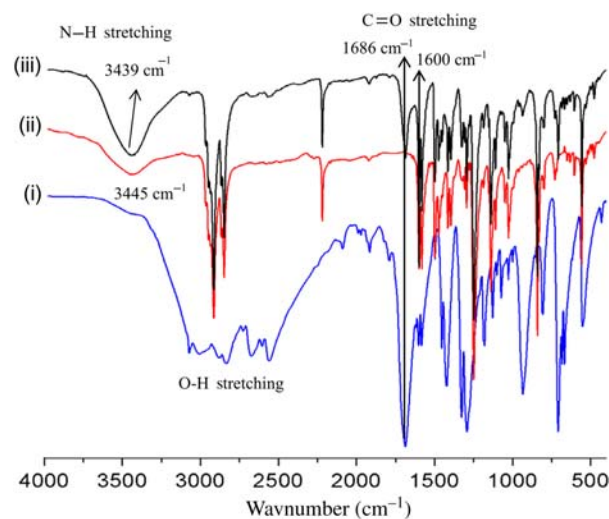


Figure 1. FT-IR spectra of (i) benzoic acid; (ii) compound **4** and (iii) hydrogen-bonded complexes **4a**.

compound **4** is presumed to be due to the spinning of the rod around the long axis suppressed by the lateral intermolecular H-bonding, which has destabilised the liquid crystal phase but stabilised the crystalline state. In addition, the intermolecular interaction between the layers increases the rigidity. The carboxylic acid derivatives are then introduced as a dopant to compound **4**, which reduces the molecular rigidity via the intermolecular reorganisation (Figure 3) (16). A noteworthy feature of this study is that both compound **4** and carboxylic acids (**a–e**) are non-mesogenic, but the resulting complexes exhibit mesomorphic properties. The complex **4a** shows SmA and N phases on heating and cooling cycles (Figure 4(a),(b)). On cooling from the isotropic phase, the N phase formed at 102.4°C and further cooling gave the SmA at 86.5°C. Both

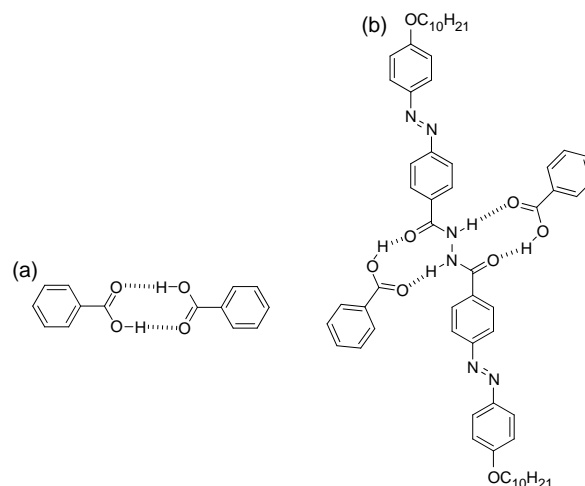


Figure 2. Intermolecular hydrogen bonds in (a) benzoic acid and (b) complex **4a**.

Table 1. Phase transition temperatures ( $^{\circ}\text{C}$ ) and enthalpies [ $\text{J g}^{-1}$ ] for series 1.

Complex	Phase transition behaviour	
	Heating	Cooling
<b>4</b>	Cr 104.7 [91.7] I	I 83.6 [86.2] Cr
<b>4a</b>	Cr 89.4 [99.2] SmA 98.2 [15.3] N 103.0 [14.8] I	I 102.4 <sup>a</sup> N 86.5 [20.5] <sup>b</sup> SmA 67.2 [74.1] Cr
<b>4b</b>	Cr 98.6 N <sup>c</sup> 108.5 [93.0] I	I 106.5 <sup>a</sup> N 91.6 [2.0] SmA 82.8 [84.2] Cr
<b>4c</b>	Cr 93.6 N <sup>c</sup> 95.5 [83.7] I	I 88.9 <sup>a</sup> N 76.0 [72.3] Cr
<b>4d</b>	Cr 79.4 [88.7] N 96.3 [42.1] I	I 80.3 [38.7] N 62.4 [83.6] Cr
<b>4e</b>	Cr 101.9 N <sup>c</sup> 104.6 [97.4] I	I 100.9 [4.2] N 96.6 <sup>a</sup> SmA 79.6 [86.3] Cr

Notes: Phase transition temperatures were determined by DSC thermogram. Cr, crystal; N, nematic; SmA, smectic A; I, isotropic phase.

<sup>a</sup>Phase transition was observed by POM and weak transition was detected by DSC in which the enthalpy change was not observed.

<sup>b</sup>Two transitions such as I–N and N–SmA enthalpies are combined.

<sup>c</sup>Phase transition was merely observed by POM wherein the mesophase range is very short that could not be detected by DSC.

the transitions I–N and N–SmA are very close to each other and hence the values of enthalpy changes are combined as  $20.5 \text{ J g}^{-1}$  (Figure 5). Complex **4b** exhibits N phase on heating, whereas on cooling it shows N and SmA phases. On heating, however, the N phase was observed by Polarized optical microscopy (POM) on very slow heating rate ( $2^{\circ}\text{C min}^{-1}$ ). It possesses very short temperature range associated with N phase, and hence the phase transition could not be detected by Differential scanning calorimetry (DSC). Complexes **4c** and **4d** display N phase on heating and cooling cycles. The low N-phase stability for complex

**4c** is found to be similar to the phenomenon that occurred in complex **4b**. This has again hindered us from using DSC to detect the phase transition N–I. This phenomenon can also be inferred from complex **4e** which exhibits short N-phase stability on heating whereas on cooling it exhibits schlieren N and focal-conic fan texture of SmA (Figure 4(c),(d)). The I–N transition was observed at  $100.9^{\circ}\text{C}$  with very low enthalpy of  $4.2 \text{ J g}^{-1}$ . Although the phase transition from N to SmA is observed at  $96.6^{\circ}\text{C}$ , the enthalpy value could not be detected by DSC. On further cooling, it crystallised at  $79.6^{\circ}\text{C}$ .

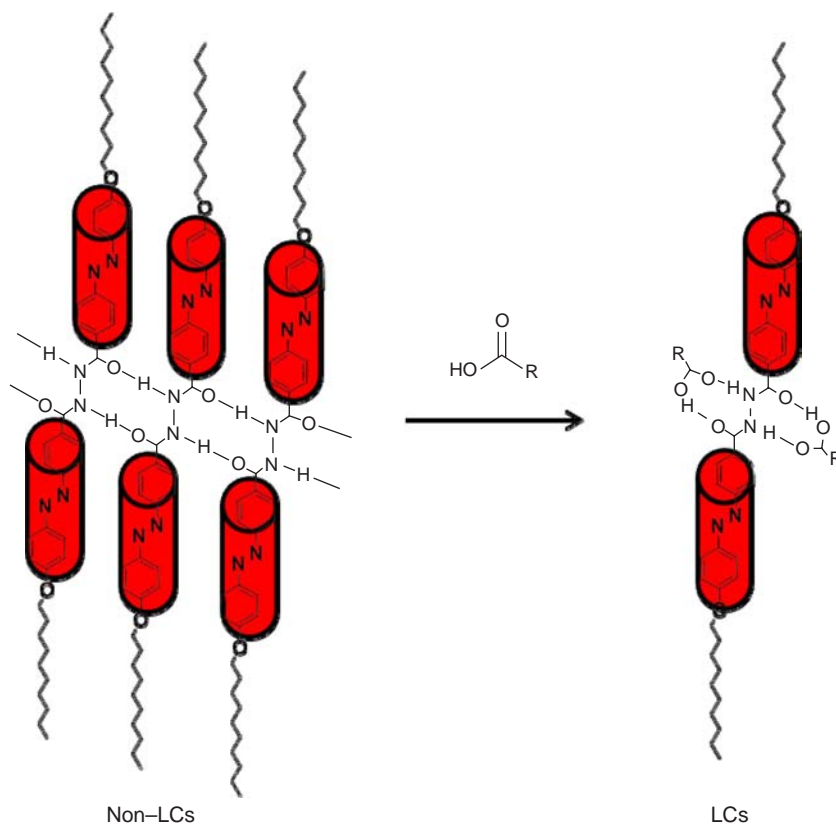


Figure 3. A diagrammatic representation for the segregation of non-liquid crystalline molecules into mesomorphic complexes by carboxylic acid dopant.

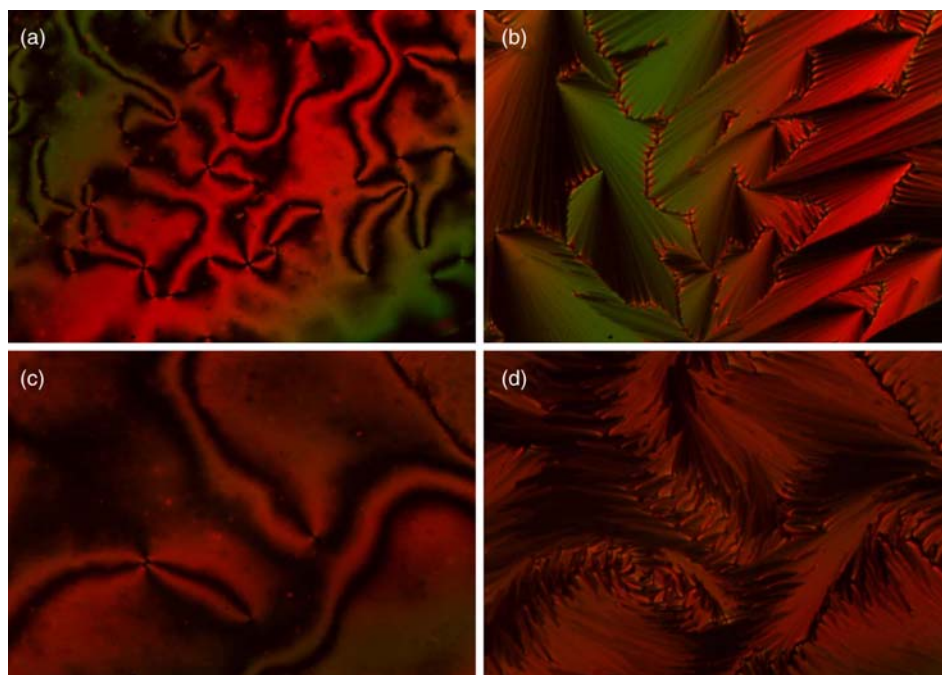


Figure 4. Photomicrographs showing (a) N phase at 98.4°C in complex **4a**, (b) SmA phase at 82.0°C in complex **4a**, (c) N phase at 99.0°C in complex **4e** and (d) SmA phase at 84.5°C in complex **4e**.

Table 2. Phase transition temperatures (°C) and enthalpies [ $\text{J g}^{-1}$ ] for series 2.

Complex	Phase transition behaviour	
	Heating	Cooling
<b>4f</b>	Cr 82.6 [77.1] SmA 121.6 [26.9] I	I 118.2 [23.6] SmA 79.8 [67.5] I
<b>4g</b>	Cr 79.2 [80.8] SmA 101.9° N 115.8 [14.6] I	I 112.5 [10.3] N 99.9 [2.1] SmA 77.0 [63.1] Cr
<b>4h</b>	Cr 62.5 [76.9] SmA 142.1 [25.5] N 177.6 [16.7] I	I 174.3 [15.6] N 140.7 [23.1] SmA 60.5 [70.8] Cr
<b>4i</b>	Cr 98.9 [106.1] N 210.0 [35.6] I	I 201.1 [27.9] N 90.7 [96.1] I
<b>4j</b>	Cr 78.4 [20.1] Cr <sub>1</sub> 116.2 [48.6] Col 141.3 [28.5] I	I 138.4 [20.1] Col 113.6 [42.6] Cr <sub>1</sub> 75.0 [16.8] Cr

Notes: Phase transition temperatures were determined by DSC thermogram. Cr, Cr<sub>1</sub>, crystal; N, nematic; SmA, smectic A; Col, columnar; I, isotropic phase.

The polarising optical microscopy and DSC thermogram are employed to study the thermal behaviour of the complexes **4f–4j**. Table 2 gives the transitional temperature and the associated enthalpies of series 2 complexes. These complexes are obtained from the reactions of non-liquid crystalline compound **4** with liquid crystalline carboxylic acid derivatives **f–j**. Moreover, the terminal chain length of the carboxylic acid was maintained as alkyl chain ( $\text{C}_{10}\text{H}_{21}$ ). All the complexes exhibit enantiotropic mesomorphism. The complex **4f** shows focal conic SmA phase (Figure 6(a)). On cooling from the isotropic phase, SmA phase is developed at 118.2°C and crystallised at 79.8°C. The compounds **4g** and **4h** exhibit dimesomorphism of N and SmA. The complex **4g** exhibits schlieren N phase at 112.5°C on cooling from isotropic phase, followed by the focal-conic SmA that can be observed at 99.9°C (Figure 6(b)) prior to

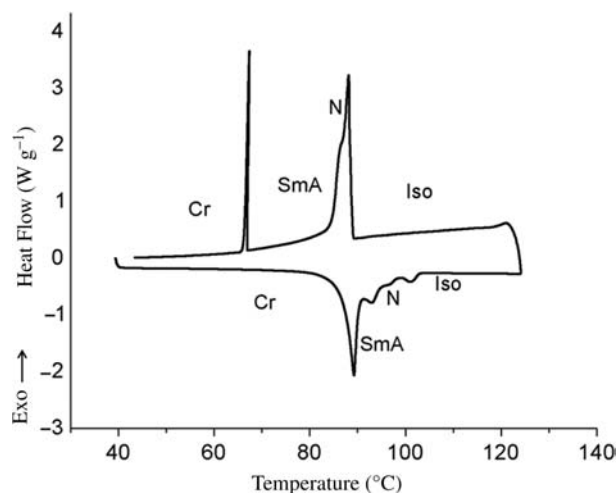


Figure 5. DSC thermogram of complex **4a**.

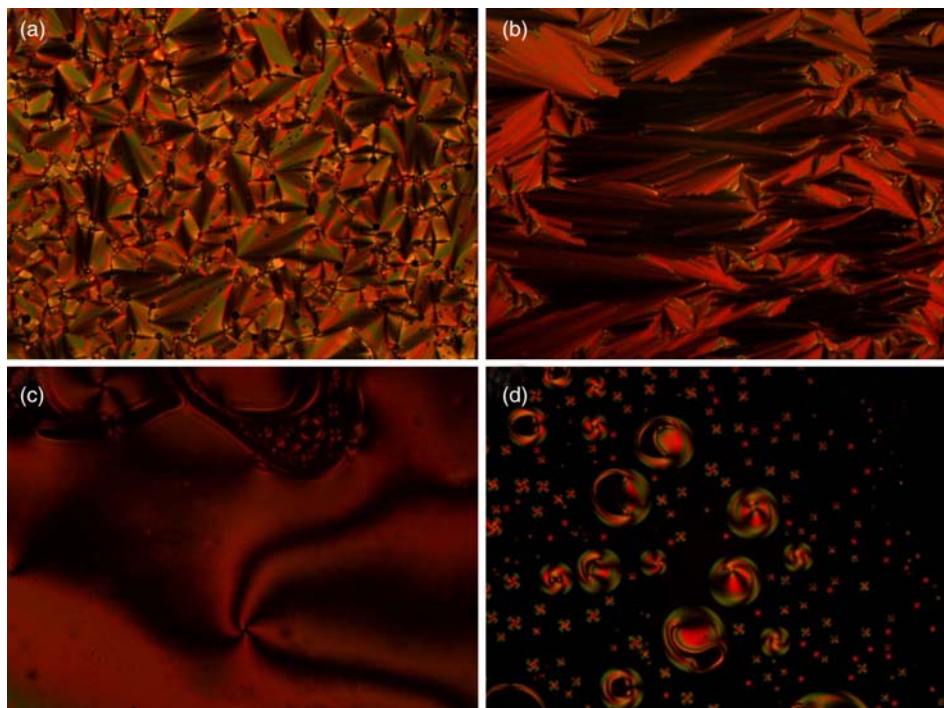


Figure 6. Photomicrographs showing (a) SmA phase at 98.4°C in complex **4f**, (b) SmA phase at 82.0°C in complex **4g**, (c) N phase at 99.0°C in complex **4h** and (d) N phase at 84.5°C in complex **4i**.

crystallisation at 77.0°C. Complex **4h** exhibits N phase at 174.3°C (Figure 6(c)). On further cooling, SmA phase observed at 140.7°C and it possesses large smectic phase temperature range ( $\Delta T_{\text{SmA}} = 80.2^\circ\text{C}$ ). As for complex **4i**, it possesses very high N-phase stability ( $\Delta T_{\text{N}} = 110.4^\circ\text{C}$ ) on cooling (Figure 6(d)).

One of the remarkable features can be ascribed to the presence of discotic columnar phase as shown by complex **4j** (Figure 7(a),(b)). On cooling from the isotropic phase, complex **4j** shows dendritic growth aggregation of a discotic columnar phase (bright) from the isotropic melt (dark) at 138.4°C (17). To establish the nature of the

proposed columnar phase, the X-ray diffraction (XRD) study was carried out on complex **4j**. The XRD pattern (1D and 2D) was shown in Figure 8(a),(b) (at 140°C upon cooling). The molecular arrangement of the rectangular columnar phase in complex **4j** is depicted in Figure 8(c) of which the  $d_1 = 4.36 \text{ nm}$  ( $2\theta = 1.8^\circ$ ) and  $d_2 = 3.41 \text{ nm}$  ( $2\theta = 2.21^\circ$ ) are the long and short axes of  $\text{Col}_r$  phase, respectively, and  $l = 0.5 \text{ nm}$  ( $2\theta = 15.4^\circ$ ) is the lateral molecular distance (11, 18). The present complex **4j** that possesses four azo linkages favours the disc-shaped arrangement as that reported for nicotinic acid derivatives (19). This observation has strongly implied that the

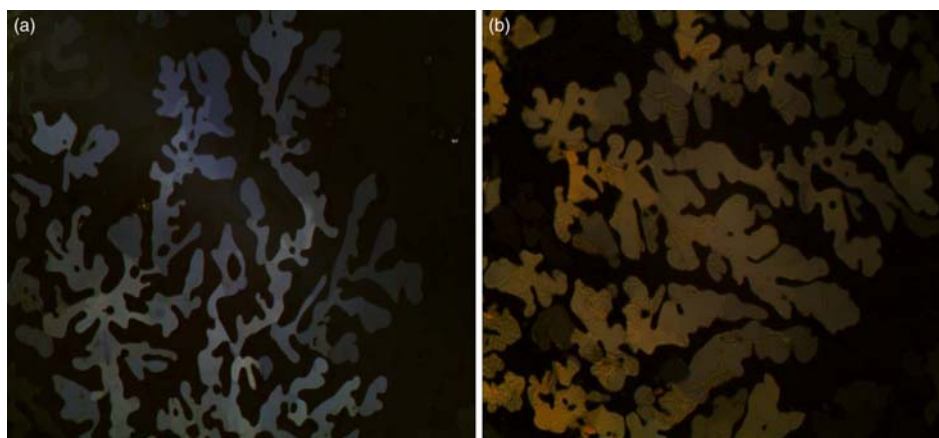


Figure 7. Photomicrographs showing columnar phase in complex **4j** at (a) 99.0°C and (b) 82.5°C.



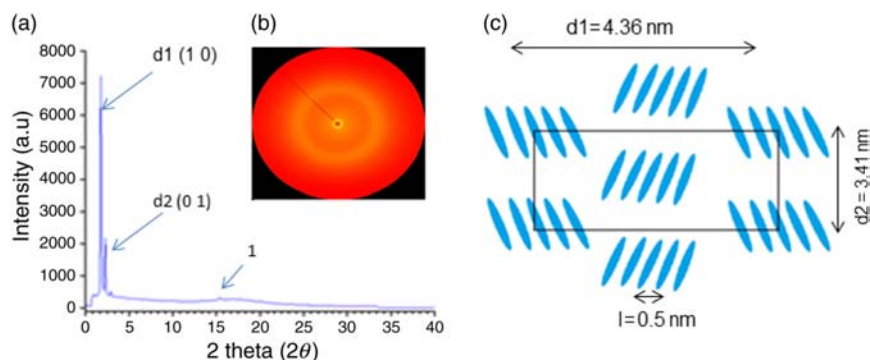


Figure 8. (a) One-dimensional XRD pattern of complex **4j** upon cooling, (b) 2D XRD patterns of complex **4j** upon cooling (at 130°C) and (c) a schematic diagram of the molecular arrangement in the rectangular columnar phase.

presence of azo linkage plays a key role in the formation of columnar phase.

#### 4. Conclusion

Intermolecular H-bonded non-liquid crystalline compound 1,2-bis[4-(4-(10-decyloxy)phenylazo)]benzoylhydrazine (**4**) and its complexes were synthesised. The thermal and optical behaviours were analysed by DSC and POM. It has been claimed that the restricted motion of the molecular spinning suppressed the liquid crystalline properties of compound **4**. The intermolecular hydrogen-bonded sites within compound **4** are found to be deteriorated through the addition of carboxylic acid. It is noteworthy that, in the first series, the non-liquid crystalline compound **4** complexed with non-liquid crystalline carboxylic acid derivatives **a–e** leading to liquid crystalline complexes. Similarly, in second series, the non-liquid crystalline compound **4** and liquid crystalline carboxylic acid derivatives **f–j** enabled the formation of liquid crystalline complexes. Generally, the ultimate complexes exhibited N and SmA phases except complex **4j** that showed predominantly columnar phase.

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