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# Columnar mesophases constructed by hierarchical self-organization of rod-like diacetylene molecules<sup>†</sup>

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We report a new class of liquid crystalline system exhibiting columnar mesophases, which are constructed by the hierarchical supramolecular self-organization of a rod-like diacetylene derivative as the primary building block. A series of 1,3-alkadiynyl-4-benzoic acids (*m*DA) with different alkyl chain lengths (m = 8-16) were synthesized and their mesophase properties were investigated by differential scanning calorimetry, polarized optical microscopy, and X-ray diffraction under temperature control. The *m*DA exhibited three types of mesophases, *i.e.*, a discotic lamellar phase, D<sub>L</sub>, and two columnar rectangular phases, Col<sub>rd</sub> and Col<sub>ro</sub>, with disordered and ordered stacking structures of the mesogens in a column, respectively, depending on the length of the alkyl substituent and temperature. We have revealed that the columnar mesophase structures are constructed with the rod-like *m*DA molecules as the starting building blocks by hierarchical self-organization. The hydrogen-bonded dimers of the carboxylic acid with a rigid framework are assembled to provide a disc-like mesogen unit, which consists of a  $\pi$ -stacked core-part and peripheral alkyl-chains. The discotic supramolecular mesogens further stack in ordered and disordered columnar structures, producing the Col<sub>ro</sub> and Col<sub>rd</sub> mesophases, or in the layer D<sub>L</sub> mesophase. This is a rare example for the discotic mesophases using the rod-like diacetylenes with a non-branched molecular structure.

## Introduction

Discotic liquid crystals with a columnar stacking structure have attracted growing interest because of their significant potential for fundamental physics and chemistry as well as applications to organic electronic devices, such as displays, light-emitting diodes, photovoltaic diodes, field effect transistors, and memories,1-5 since the first identification of the liquid crystal composed of discshaped molecules in 1977 by Chandrasekhar et al.6 The molecular structure of mesogens used for the discotic liquid crystals usually implies a rigid aromatic core and flexible alkyl chains surrounding the core. A large number of the discotic mesogens, such as substituted benzenes,<sup>6,7</sup> triphenylenes,<sup>8</sup> porphyrins,<sup>9</sup> and phthalocyanines,<sup>10</sup> have been synthesized in order to investigate their mesophase structure as well as the physical properties. Since the late 1980s, supramolecular liquid crystals using a well-defined mesogenic complex constructed by complementary intermolecular hydrogen bonding between different molecules have been

investigated by Kato and Fréchet,<sup>11</sup> Lehn *et al.*,<sup>12</sup> and other groups.<sup>13–15</sup> Columnar liquid crystalline properties for heteromeric hydrogen bonded systems using supramolecular mesogens with a pseudo disc-like shape have been revealed.<sup>16</sup>

Other types of mesogens having a non-disc structure are also used as the building blocks for the discotic and columnar liquid crystals. Phasmids and biforked molecules with a rod-like rigid core with two half-disc moieties at the ends, called polycatenar mesogens, based on their molecular structures, exhibit a columnar mesophase.<sup>17</sup> An increase in the number of flexible alkyl chains bound to the inner rigid core of polycatenars leads to breaking of the nematic or lamellar (smectic) mesophase structure and forming a ribbon-like aggregate, being further organized to form cubic and columnar mesophase structures. Another rod-like compound exhibiting a columnar phase is the polygonal cylinder molecule, in which an increase in the volume of the flexible chain in the mesogen induces the formation of nonlamellar mesophases, i.e., columnar, cubic, and the other 3D ordered one.18 The rod-coil and coil-rod-coil molecules consisting of an aromatic rigid part and poly(ethylene oxide) coils also prefer cubic and hexagonal columnar structures.<sup>19</sup>

An early example of mesophase formation by hydrogen bonding is that of the alkoxy- and alkyl-substituted benzoic acids and related compounds, which form a hydrogen-bonded dimer.<sup>20–23</sup> Hydrogen bonding between carboxylic acids generates a long lath-like structure consisting of successive conjugating units as the rigid core, exhibiting a nematic or smectic phase.

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A rigid diacetylene moiety is also used as the core part of the mesogen for the construction of nematic, lamellar, and columnar liquid crystals,<sup>24</sup> for example, a micellar triclinic mesophase is obtained by the supramolecular assembly of phasmid-type diacetylene molecules.<sup>25</sup> Recently, we found that 1,3-icosadiynyl-4-benzoic acid, which has a simple and linear molecular structure consisting of rigid aromatic and diacetylene units and a flexible alkyl chain, exhibits a highly ordered liquid crystalline state in the temperature range of 100-180 °C.<sup>26</sup> In the present study, we have synthesized 1,3-alkadiynyl-4-benzoic acids (mDA) with different alkyl chain lengths (m = 8-16 in Scheme 1), and investigated their liquid crystalline properties using differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD) under temperature control. We now report a new class of discotic liquid crystal system, which is constructed by the hierarchical supramolecular self-organization of the disc-shape mesogen consisting of a rod-like diacetylene derivative as the primary building block.

#### **Results and discussion**

#### Mesophase behaviors

All the mDAs were prepared by the Cadiot-Chodkiewicz coupling reaction of the corresponding 1-iodo-1-alkynes with 4-ethylbenzoic acid<sup>27</sup> (see ESI<sup>†</sup>). The synthetic route of the mDAs is shown in Scheme 1.

The phase transition temperatures and their enthalpy changes for the mDAs are listed in Table 1. Fig. 1 shows the phase diagrams versus the alkyl chain lengths (m) of the mDAs during the heating and cooling processes. Each compound showed a crystalline phase  $(K_1)$  at room temperature and underwent a crystal-to-crystal phase transition before reaching a mesophase upon heating. The 8DA melted at 186.6 °C and provided the isotropic liquid (IL) state without showing any mesophase after the three-step crystal-to-crystal phase transitions. When the *m***DA**s with m = 9-11 were heated, the crystalline K<sub>2</sub> or K<sub>3</sub> phase transformed into a mesophase at 157.7, 145.9, and 148.6 °C, for 9DA, 10DA and 11DA, respectively. Upon further heating, the mesophase cleared into the IL state at 184.6, 183.5, and 176.3 °C, respectively. For 12DA-16DA with larger alkyl substituents, the crystalline K<sub>3</sub> or K<sub>4</sub> state first changed into a mesophase at 117.3-139.1 °C, then transformed into the other type of mesomorphic structure at 152.0-156.8 °C, and finally the phase cleared into the IL state at 165.2-172.6 °C. The mesophase structures observed during a heating process are assigned as columnar rectangular phases (Col<sub>r</sub>) and a discotic lamellar phase  $(D_{I})$ , as described later.

When the mDAs were cooled from the IL state, they transformed into the D<sub>L</sub> phase for all the compounds except 8DA. For **9DA**, the  $D_L$  phase was directly crystallized to give  $K_2$ , but all the other compounds 10DA-16DA changed once into the Col<sub>rd</sub> phase. During the further cooling process, another phase, Col<sub>ro</sub>, was observed for 10DA-13DA before crystallization, while 14DA and 16DA were directly crystallized from the Col<sub>rd</sub> phases, resulting in the K<sub>3</sub> phase. Here, Col<sub>rd</sub> and Col<sub>ro</sub> are the columnar rectangular phases with disordered and ordered stacking structures of the mesogens in a column, respectively. The crystal phase  $(K_2 \text{ or } K_3)$  produced by the crystallization from the liquid crystalline states upon cooling was stable enough to remain at a lower temperature without any further crystal-to-crystal transition into another crystalline phase ( $K_1$  or  $K_2$ ). These reversible and irreversible steps for the phase transitions are confirmed by the DSC traces and the POM observation (Fig. 2).

Some of the Col<sub>ro</sub> and Col<sub>rd</sub> phases were not observed during the heating process because of a superheating occurrence.<sup>28</sup> This can be rationally explained by the Gibbs energy-temperature (G-T) diagram. The results for 10DA and 13DA are shown in Fig. 3 as typical examples. When the phase transition from K to Col<sub>ro</sub> is obstructed by the superheating, the remaining K portion undergoes a direct phase transition from K to Col<sub>rd</sub>. This case is applied to 12DA and 13DA. The phase transition from K to Colro at 123 °C is not observed, and the transition to Colrd occurs at 135 °C for 13DA as shown in Fig. 3(a). Moreover, if the phase transition from not only K to Colro, but also Colro to Colrd does not occur by superheating, the remaining K can undergo the phase transition to  $D_L$ , as seen for **10DA** and **11DA** [Fig. 3(b)]. When the phase transition temperatures are close to each other, the superheating tends to readily occur. If the heating is carried out at an infinitely low scanning rate, the Col<sub>ro</sub> and Col<sub>rd</sub> phases may appear, although no additional mesophase was observed at the heating rate of 2-10 °C min<sup>-1</sup>.

Fig. 4 shows the typical optical textures observed for the mesophases of the 10DA, which were observed during the cooling process from the IL state by POM. We can clearly see a dendritic texture, which is characteristic of a discotic mesophase, at 182 °C. A focal-conic texture and a terrace structure, which are characteristics of a lamella structure, are also seen in this mesophase. During further cooling, the dendritic aggregates and the focal-conic fan textures transformed into a mosaic texture, as observed in the photograph for the Col<sub>rd</sub> phase. A terrace structure was more clearly observed for the Col<sub>rd</sub> phase than for the D<sub>L</sub> phase. The optical textures of the two Col<sub>r</sub> phases were close to each other, but a striated texture was additionally observed in the Colro phase [Fig. 4(c)].

#### **X-Ray diffractions**

We carried out the XRD experiments in order to accurately determine the mesophase structures. Fig. 5 shows the XRD profiles for 13DA recorded at 166, 152, and 135 °C, which correspond to the  $D_L$ ,  $Col_{rd}$ , and  $Col_{ro}$  phases, respectively. Table 2 summarizes the lattice constants for the possible mesophase structures and the observed and calculated d-spacing values for 13DA as well as the assignment of the Miller indices for each diffraction line (see ESI<sup>†</sup> for the XRD data for the all mDAs).



**Table 1** Phase transition temperatures  $(T/^{\circ}C)$  and enthalpy change  $(\Delta H/kJ \text{ mol}^{-1} \text{ in brackets})$  for the **mDAs**<sup>*a*</sup>

compounds	l.		pha	ase <u></u>	[ΔH/	kJ mol <sup>-1</sup> ] →	pha	se			
8DA	K1	48.8 [0.13]	K2	117.8 [0.58] 145.8 [1.37]	K <sub>3</sub>	153.2 [2.19] 161.5 [0.42]	K₄	186.6 [20.7] 184.0 [11.7]	<u> </u>	L	
9DA	κ	51.5 [8.41]	K <sub>2</sub>	157.7 [6.90] 152.9 [5.60]	DL	184.6 [17.7]	IL				
10DA	K1	60.4 [17.7]	K2	145.9 [4	4.97]	₹ D <sub>L</sub> ₹	183.5 180.4	[15.7] ■ IL [11.1]			
[3.81] Col <sub>ro</sub> ← Col <sub>rd</sub> [0.17]											
		43.0 [1.82]		149.9 [l 50.9 [15.9]	0.14]	148.6 [8	3.03]		176	.3 [15.6]	
11DA	K <sub>1</sub>		K <sub>2</sub>	142	K3	<b>∢</b> ∢			<b>▲</b> 177	.3 [11.6] IL	
				[6.6	3]	Col <sub>ro</sub>	0.10]	Col <sub>rd</sub> [0.20	)]		
12DA	K <sub>1</sub>	35.8 [1.85]	K2	62.5 [23.9]	K <sub>3</sub>	139.1 [7.01]	iol <sub>rd</sub> 🚽	155.5 [0.15]	DL	172.6 [16.0]	IL
				12 [6.	7.8 26]	Col <sub>ro</sub> [0.	7.8 03]	157.4 [0.22]		175.7 [12.4]	
13DA	K₁/K₂	48.1 [12.6]	K3	70.1 [14.3]	K4 -	135.3 [8.73]	ol <sub>rd</sub> –	156.8 [0.11]	DL	168.4 [18.6]	IL
				12 [7.	3.0 96]	Col <sub>ro</sub> [0.	6.2 05]	158.1 [0.17]		173.3 [12.3]	
1404	к.	62.1 [8.50]	к.	77.7 [16.7]	к.	123.2 [8.39]	ol. –	154.8 [0.22]	D.	169.3 [16.2]	
1404	••1				. •3	109.0 [8.47]	rd <	156.6 [0.27]	υL	172.5 [15.6]	
16DA	K <sub>1</sub>	54.4 [7.54]	K <sub>2</sub>	89.1 [17.4]	K <sub>3</sub>	117.3 [9.50] ▲ ▲ C	ol <sub>rd</sub>	152.0 [0.27]	DL	165.2 [15.8]	IL
						106.0 [9.38]		154.2 [0.29]		169.7 [15.0]	

<sup>*a*</sup> Phase nomenclature:  $K_1$ ,  $K_2$ ,  $K_3$ , and  $K_4$  = crystals,  $Col_{ro}$  and  $Col_{rd}$  = columnar rectangular phases,  $D_L$  = discotic lamellar phase, and IL = isotropic liquid.

Fig. 6 is a schematic representation for the possible packing structures of discotic mesogens in the columnar mesophases. In a columnar mesophase, discotic mesogens assemble themselves to form a column perpendicular to a 2D lattice plane. In general, the columnar mesophases are classified based on the 2D lattice symmetry of the column packing as follows: (a) columnar hexagonal phase (Col<sub>h</sub>), (b) columnar tetragonal phase (Col<sub>tet</sub>), (c) columnar oblique phase (Col<sub>ob</sub>), and (d) columnar rectangular phase (Col<sub>r</sub>). The Col<sub>r</sub> phases further divide into four types by the 2D lattice symmetry. Each phase implies the ordered and disordered stacking of the mesogens in a column represented by the subscripts o and d, respectively.

In Fig. 5(a) and (b), the D<sub>L</sub> phase of **13DA** showed a series of diffractions due to the 00l planes in a small angle region  $(2\theta = 2-8^{\circ})$ , which are characteristics to a lamellar structure. In addition, a weak diffraction was observed at a larger angle  $(2\theta = 18.04^{\circ})$ , d = 4.91 Å) as well as broad diffractions at 10–30°.<sup>9b,29</sup> The Col<sub>r</sub> phases observed at 152 and 135 °C showed another series of diffraction lines in a small angle region. The lines observed around 2–6° are assigned to the diffractions due to the (110), (020), (220), and (130) planes for the lattice with a = 54.63 Å and b = 47.99 Å for the Col<sub>rd</sub> phase and a = 57.68 Å and b = 46.73 Å for the Col<sub>ro</sub> phase [Fig. 5(c) and (d)]. The weak diffractions

observed at larger angles ( $2\theta = 7-15^{\circ}$ ) were also assigned based on the comparison of the observed and calculated *d*-spacing values, as shown in Table 2. The extinction rule for rectangular lattices suggests a Col<sub>r</sub> phase with  $P2_1/a$  symmetry for the both structures observed at 152 and 135 °C.

In this study, if **mDA** prefers any smectic mesophase, such as the smectic B and E phases, a sharp and strong diffraction due to the alkyl chain stacking should appear at the position corresponding to the *d*-value of *ca.* 4 Å. In this study, such diffraction was not observed [Fig. 5(a)]. Instead, other weak diffraction lines were observed, which are assigned as diffractions due to the columnar stacking of the discotic mesogens ( $h_A$  and  $h_B$ ). Similar characteristic lines were observed in the XRD profiles of **10DA– 12DA**, independent of the length of the alkyl chain (see ESI<sup>†</sup>).

In Fig. 7, each lattice constant for the mesophase structures is plotted as a function of the carbon number of the alkyl chain. The *a*-axis values linearly increased with an increase in the alkyl chain length, while the *b*-axis values were almost constant. This suggests that the direction of the expansion of the alkyl domains is always along the *a*-axis direction. The plots of the lattice length of the *a*- and *b*-axes of the **16DA** mesophases deviated from the linear relationship for the  $D_L$  and  $Col_{rd}$  phases. This suggests enhanced interaction between the long-alkyl chains. For **14DA** 



**Fig. 1** Phase transition temperatures *versus* the alkyl-chain length (*m*) of the *m***D**As determined during (a) the heating process and (b) the cooling process by DSC. The crystalline samples were obtained by recrystallization from a mixture of tetrahydrofuran and methanol and used for the DSC measurements.

and **16DA**, the  $\text{Col}_{ro}$  (*P*2<sub>1</sub>/*a*) phase with an ordered columnar stacking was not detected. This is due to the fact that long alkylchains prefer a robust lamellar packing structure with a fully expanded (*trans* zigzag) conformation in the crystalline state than a highly ordered alignment of the discs in the mesophases.

The enthalpy changes determined by DSC (Table 1) also support the assignment of these mesophase structures. High  $\Delta H$  values (11.1–15.6 kJ mol<sup>-1</sup>) were observed for the transition from the IL state to the D<sub>L</sub> phase, and the relatively small one for the D<sub>L</sub> to Col<sub>rd</sub> transition ( $\Delta H = 0.17$ –0.29 kJ mol<sup>-1</sup>). A slight change in the local structure during the disordered-to-ordered transition of the Col<sub>r</sub> phase has resulted in the lowest  $\Delta H$  values ( $\Delta H = 0.03$ –0.14 kJ mol<sup>-1</sup>).



Fig. 2 DSC traces of (a) **10DA** and (b) **12DA**. The heating and cooling rates are  $10 \degree C \min^{-1}$ .



Fig. 3 Schematic G-T (Gibbs energy-temperature) diagrams for (a) **13DA** and (b) **10DA**. Symbols indicate the transitions observed during ( $\bigcirc$ ) both heating and cooling processes, ( $\square$ ) only heating process and ( $\bullet$ ) only cooling process.

#### Molecular stacking

In the diffraction profile of **13DA** at the Col<sub>ro</sub> phase [Fig. 5(d)], two weak diffractions were detected at  $2\theta = 21.59$  and  $23.32^{\circ}$ (d = 4.11 and 3.81 Å, respectively) in addition to the line



**Fig. 4** Optical textures observed for the mesophases of **10DA** during the cooling process from the IL state. (a)  $D_L$  phase at 182 °C, (b)  $Col_{rd}$  phase at 159 °C and (c)  $Col_{ro}$  phase at 150 °C.



Fig. 5 XRD profiles of 13DA for (a, b)  $D_L$  phase at 166 °C, (c)  $Col_{rd}$  phase at 152 °C and (d)  $Col_{ro}$  phase at 135 °C.

observed at 4.82 Å, while the  $\operatorname{Col}_{rd}$  phase gave only the single diffraction of 4.86 Å [Fig. 5(c)]. The two additional diffractions observed in a wider angle region are due to the alignment of the disc-shaped mesogens in a column. The line corresponding to d = 4.1 Å is assigned as the diffraction due to the core parts ( $h_A$ ), while that observed at 3.8 Å is due to the alkyl-chain stacking ( $h_B$ ), as illustrated in Fig. 8. The  $h_A$  value observed for the Col<sub>ro</sub> phase was constant as 4.1 Å, being higher than that of the expected values (3.5 Å) for the  $\pi$ - $\pi$  stacking with the face-to-face interaction of the aromatic cores and independent of the *m* value. Thus is due to the edge-to-edge type stacking of the mesogens in a column. The  $h_B$  value slightly increased from 3.71 to 3.81 Å with an increase in the *m* value from 10 to 13 (see Table S1 in ESI†) due to the steric repulsion of the fluctuating alkyl chains in the mesophases.

Table 2 Assignment of XRD data for the 13DA mesophase

	Spacing		
Mesophase structure	$d_{\rm obs}/{ m \AA}$	$d_{ m calcd}/{ m \AA}$	Miller indices
D <sub>I</sub> at 166 °C. $a = 35.01$ Å	35.01	35.01	(001)
	17.35	17.50	(002)
	11.58	11.67	(003)
	4.91		
$\operatorname{Col}_{\mathrm{rd}}(P2_1/a)$ at 152 °C,	36.06	36.06	(110)
a = 54.63  Å, b = 47.99  Å	24.00	24.00	(020)
,	17.83	18.03	(220)
	15.50	15.35	(130)
	11.07	10.99	(240)
	6.56	6.65	(270)
	4.86		. ,
$\operatorname{Col}_{ro}(P2_1/a)$ at 135 °C,	36.31	36.31	(110)
a = 57.68 Å, $b = 46.73$ Å,	23.36	23.36	(020)
$Z = 18.87$ for $\rho = 1.0$ g cm <sup>-3</sup>	18.00	18.16	(220)
	15.52	15.04	(130)
	11.10	10.83	(240)
	6.51	6.50	(270)
	4.82		
	4.11		$h_{\rm A}$
	3.81		$h_{\rm B}$



**Fig. 6** Representation for the possible packing structures of discotic mesogens in the columnar mesophases. (a) Columnar hexagonal (Col<sub>h</sub>), (b) columnar tetragonal (Col<sub>tet</sub>), (c) columnar oblique (Col<sub>ob</sub>), and (d) columnar rectangular (Col<sub>r</sub>) phases.

For the Col<sub>ro</sub> phase, the Z values are estimated as 15–19 with the assumption that the density ( $\rho$ ) is equal to unity. In this case, two discs are included in each unit cell, as shown in Fig. 6(d). Accordingly, 7.5–9.5 **mDA** molecules, which correspond to 4–5 dimers, are included in each disc. It is noted that the Z value increased with an increase in the alkyl chain length of the substituent of the **mDAs** (see Table S1 in ESI†) because of an increase in the molecular stacking force. Fig. 9 shows a schematic illustration for the construction of mesophase structures by the hierarchical self-organization of the rod-like diacetylene molecules.

First, a pair of hydrogen-bonded carboxylic acids (*i.e.*, a carboxylic acid dimer) is formed. The **mDA** dimer has a rigid framework consisting of the successive diacetylene, *p*-phenylene, and carboxylic acid dimer moieties. The dimers are self-assembled and form a disc-like structure, which consists of a  $\pi$ -stacked core part and peripheral alkyl-chains. The flexible alkyl-chains fluctuate in the mesophases. The dimer stacking distance was 4.78–4.88 Å for the Col<sub>r</sub> phases and 4.91–5.04 Å for the D<sub>L</sub> phases. This suggests that the  $\pi$  stacking interaction in the core of the D<sub>L</sub> phase is smaller than that in the Col<sub>r</sub> mesophases [see also Fig. 7(d)]. The disc-like mesogens produced by the dimer stacking are further assembled to form columnar and lamellar mesophases, Col<sub>r</sub> and D<sub>L</sub>, depending on the temperature and the *m* values.

In the IR spectra of the *m*DAs, the characteristic peaks due to the C=O stretching were observed at 1741 and 1700 cm<sup>-1</sup> at 180 °C [Fig. 10(a)], indicating that some carboxyl groups are connected to each other to form a dimer by hydrogen bonding, while the others are free in the isotropic state. The intensity of the peak due to the free carboxylic acid at 1741 cm<sup>-1</sup> decreased and that of the peak due to the dimer formation at 1700 cm<sup>-1</sup>



**Fig. 7** Lattice constants *versus* alkyl-chain length, *m*, of *m*DAs. ( $\bigcirc$ ) *a*-axis and ( $\bigcirc$ ) *b*-axis values in the (a) D<sub>L</sub>, (b) Col<sub>rd</sub>, and (c) Col<sub>ro</sub> phases. (d) Other molecular stacking distance in the ( $\Box$ ) D<sub>L</sub>, ( $\blacktriangle$ ) Col<sub>rd</sub>, and ( $\diamondsuit$ ) Col<sub>ro</sub> phases.

increased during the cooling process from the IL state to the mesophases. No free carboxyl group was included in the crystalline state at 100 °C. Thus the IR spectra support the formation of a robust hydrogen-bonded dimer of the diacetylene molecules in the mesophases. The fact that similar fluorescence spectra [Fig. 10(b)] as well as UV-vis absorption spectra ( $\lambda_{max} = 299$  nm) were observed for **mDA** independent of the mesophase structures suggests that each mesophase implies a similar packing structure of the phenylene groups. We further investigated the possibility



**Fig. 8** (a) Possible stacking structure of discotic mesogens with a rigid core and flexible alkyl chains in a column and (b) molecular stacking appropriate for the polymerization. The  $h_A$  and  $h_B$  are stacking distances of the core and alkyl chain, respectively. The dimers are required to stack with a stacking distance ( $d_s$ ) of 4.8–5.0 Å and a stacking angle of *ca.* 45° in a disc for the polymerization to occur.



mDA molecule

Fig. 9 Schematic illustration showing construction of mesophase structures by hierarchical self-organization of *m*DA molecules.

of the mesophase formation using the methyl ester of mDA in order to check the role of a carboxylic acid moiety in the dimer formation. As a result, the methyl ester of **12DA** did not show any transition peak below 200 °C except for a melting point at 32.0 °C. This result supports the fact that the dimer formation is indispensable for the appearance of the mesophase characteristics in the mDA series.



Fig. 10 (a) Temperature-dependent IR spectrum of 12DA during the cooling process from 200 to 80 °C at the cooling rate of 2.5 °C min<sup>-1</sup>. Each spectrum was recorded at 4 min intervals. (b) Temperature-dependent fluorescence spectrum of 12DA.

**Table 3** Polymerization of 12DA in liquid crystalline and crystallinestates<sup>a</sup>

Phase	Temperature/°C	$M_{ m n}  imes 10^{-3}$	$M_{ m w}  imes 10^{-3}$	$M_{\rm w}/M_{\rm n}$	
D <sub>L</sub> Col <sub>rd</sub> Col <sub>ro</sub> K	165 155 145 r.t.	1.38 1.84 1.82	1.76 2.26 2.10	1.27 1.23 1.16	

<sup>*a*</sup> Polymerization conditions: UV irradiation for 5 min in the liquid crystalline states or 400 kGy  $\gamma$ -ray irradiation in the crystalline state. <sup>*b*</sup> The highly crystalline and high-molecular-weight polymers were produced, being insoluble in tetrahydrofuran.

The photopolymerization of 12DA at different temperatures corresponding to the three kinds of liquid crystalline states resulted in the formation of oligomers with the molecular weights of  $1.4-1.8 \times 10^3$ , as shown in Table 3. This is in contrast to the production of a highly crystalline and insoluble polymer during the solid-state polymerization under  $\gamma$ -ray radiation.<sup>30</sup> The molecular weight of the produced oligomers in the mesophases corresponds to the polymerization degree of 4-6, agreeing well with the aggregation number of the dimers in a disc. It is assumed that the diacetylene dimers have a stacking structure similar to that appropriate for the solid-state polymerization,<sup>31,32</sup> that is, the stacking distance ( $d_s$ ) of 5 Å and the stacking angle of 45°, as shown in Fig. 8. The propagation occurs within a disc, resulting in the formation of an oligomer, but not a high polymer. This result indicates the formation of a compartmentalized disc assembly, which is stable even in the discotic lamellar mesophase. No transition to the non-discotic phase, such as a smectic or nematic one, occurred due to the robust structures of the assemblies. The stable discs in the mesophases resulted in the oligomer formation with the noted molecular weights, which correspond to the number of mesogens aggregated in a disc. The liquid crystalline properties were revealed to vanish after the complete polymerization (oligomerization) because of the thermodynamic properties of the liquid crystalline system sensitive to the molecular structure of the mesogens. Previously, Busico et al.<sup>33</sup> reported a mesophase with a bidimensional rectangular structure of lithium n-hexadecanoate, which is also one of linearshape molecules as the building blocks for higher-order mesophase appearance. More recently, we further observed the mesomorphic properties of other related compounds including dienylene, phenylene and carboxylic acid moieties in the core part of the mesogens. Further properties of the mesomorphic systems using the unsaturated molecules, such as diacetylene and diene compounds with a carboxylic group, are continuingly being investigated.

# Conclusions

We have demonstrated in the present study the discotic mesophase system consisting of rod-like and linear diacetylene molecules as the building blocks. The liquid crystalline system is constructed by the hierarchical self-organization of the components. First, the hydrogen-bonded dimers of the carboxylic acid derivatives are self-assembled to form a disc-shape mesogen. The disc consists of a  $\pi$ -stacked core part with a rigid framework and peripheral flexible alkyl chains. The discotic mesogens further stack in a columnar or layer structure. While the carboxylic acids having a simple and calamitic molecular structure reported in the literature exhibited only nematic and smectic mesophases,<sup>20–23</sup> our present study revealed that the columnar and layer mesophases are thermodynamically favored even when linear and rod-like molecules are used as the starting building blocks for the supramolecular liquid crystalline system.

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### References

- Handbook of Liquid Crystals, ed. D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill, Wiley-VCH, Weinheim, 1998, vol. 2A and 2B.
- 2 P. S. Pershan, *Structure of Liquid Crystal Phases*, World Scientific, Singapore, 1988.
- 3 S. Chandrasekhar, *Liquid Crystals*, Cambridge University Press, Cambridge, 2nd edn, 1992.
- 4 P. J. Collings and M. Hird, *Introduction to Liquid Crystals: Chemistry* and *Physics*, Taylor & Francis, London, 1997.
- 5 Recent reviews: (a) S. Kumar, Chem. Soc. Rev., 2006, 35, 83–109; (b) T. Kato, N. Mizoshita and K. Kishimoto, Angew. Chem., Int. Ed., 2006, 45, 38–68; (c) S. Sergeyev, W. Pisula and Y.-H. Geerts, Chem. Soc. Rev., 2007, 36, 1902–1929; (d) C. Tschierske, Chem. Soc. Rev., 2007, 36, 1930–1970; (e) Y. Shimizu, K. Oikawa, K. Nakayama and D. J. Guilon, Mater. Chem., 2007, 17, 4223–4229; (f) S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, Angew. Chem., Int. Ed., 2007, 46, 4832–4887; (g) J. W. Goodby, I. M. Saez, S. J. Coeling, V. Görtz, M. Draper, A. W. Hall, S. Sia, G. Cosquer, S. E. Lee and E. P. Raynes, Angew. Chem., Int. Ed., 2008, 47, 2754–2787.
- 6 S. Chandrasekhar, B. K. Sadashiva and K. A. Suresh, *Pramana*, 1977, 9, 471–480.
- 7 (a) I. Tabushi, K. Yamamura and Y. Okuda, J. Org. Chem., 1987, 52, 2502–2505; (b) D. M. Collard and C. P. Lillya, J. Am. Chem. Soc., 1989, 111, 1829–1830; (c) C. Pugh and V. Percec, J. Mater. Chem., 1991, 1, 765–773; (d) J. Y. Chang, J. R. Yeon, Y. S. Shin, M. J. Han and S. K. Hong, Chem. Mater., 2000, 12, 1076–1082; (e) S. Ito, M. Ando, A. Nomura, N. Morita, C. Kabutom, H. Mukai, K. Ohta, J. Kawakami, A. Yoshizawa and A. Tajiri, J. Org. Chem., 2005, 70, 3939–3949.
- 8 (a) C. Destrade, N. H. Tinh, H. Gasparoux, J. Malthête and A. M. Levelut, Mol. Cryst. Liq. Cryst., 1981, 71, 111-135; (b) C. Piechocki, J. Simon, A. Skoulios, D. Guillon and P. Weber, J. Phys. Chem. A, 1982, 104, 5245-5247; (c) A. M. Levelut, P. Oswald, A. Ghanem and J. Malthête, J. Phys. (Paris), 1984, 45, 745-754; (d) D. R. Beattie, P. Hindmarsh, J. W. Goodby, S. D. Haslam and R. M. Richardson, J. Mater. Chem., 1992, 2, 1261-1266; (e) H. Bengs, F. Class, T. Frey, D. Funhoff, H. Ringsdorf and K. Siemensmeyer, Liq. Cryst., 1993, 15, 565-574; (f) N. Boden, R. C. Borner, R. J. Bushby, A. N. Cammidge and M. V. Jesudason, Liq. Cryst., 1993, 15, 851-858; (g) D. Adams, P. Schuhmacher, J. Simmerer, L. Häussling, K. Siemensmeyer, K. H. Etzbach, H. Ringsdorf and D. Haarer, Nature, 1994, 371, 141-143; (h) J. A. Rego, S. Kumar and H. Ringsdorf, Chem. Mater., 1996, 8, 1402-1409; (i) F. Charra and J. Cousty, Phys. Rev. Lett., 1998, 80, 1682-1685; (j) L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend and J. D. MacKenzie, *Science*, 2001, **293**, 1119–1122; (k) N. Terasawa, H. Monobe, K. Kiyohara and Y. Shimizu, Chem. Commun., 2003, 1678-1679; (1) S. Kumar, Liq. Cryst., 2004, 31, 1037-1059; (m) S. Kumar, Liq. Cryst., 2005, 32, 1089-1113.

- 9 (a) P. G. Schouten, J. M. Warman, M. P. Dehaas, M. A. Fox and H. L. Pan, Nature, 1991, 353, 736–737; (b) A. M. Giroud-Godquin and P. M. Maitlis, Angew. Chem., Int. Ed., 1991, 30, 375–402; (c) F. Lelj, G. Morelli, G. Ricciardi, A. Roviello and A. Sirigu, Liq. Cryst., 1992, 12, 941–960; (d) Y. Shimizu, M. Miya, A. Nagata, K. Ohta, I. Yamamoto and S. Kusabayashi, Liq. Cryst., 1993, 14, 795–805; (e) K. Ohta, N. Yamaguchi and I. Yamamoto, J. Mater. Chem., 1998, 8, 2637–2650; (f) C. Y. Liu, A. Fechtenkotter, M. D. Watson, K. Müllen and A. J. Bard, Chem. Mater., 2003, 15, 124–130.
- 10 (a) D. Markovitsi, I. Lecuyer and J. Simon, J. Phys. Chem., 1991, 95, 3620–3626; (b) P. G. Schouten, J. M. Warman, M. P. de Haas, C. F. van Nostrum, G. H. Gelinck, R. J. M. Nolte, M. J. Copyn, J. W. Zwikker, M. K. Engel, M. Hanack, Y. H. Chang and W. T. Ford, J. Am. Chem. Soc., 1994, 116, 6880–6894; (c) G. J. Clarkson, N. B. Mckeown and K. E. Treacher, J. Chem. Soc., Perkin Trans. 1, 1995, 1817–1823; (d) C. F. van Nostrum and R. J. M. Nolte, Chem. Commun., 1996, 2385–2392; (e) J. A. Duro, G. dela Torre, J. Barbera, J. L. Serrano and T. Torres, Chem. Mater., 1996, 8, 1061–1066; (f) J. M. Kroon, R. B. M. Koehorst, M. van Dijk, G. M. Sanders and E. J. R. Sudhölter, J. Mater. Chem., 1997, 7, 615–624; (g) M. Kimura, T. Muto, H. Takimoto, K. Wada, K. Ohta, K. Hanabusa, H. Shirai and N. Kobayashi, Langmuir, 2000, 16, 2078–2082.
- 11 (a) T. Kato and J. M. J. Fréchet, J. Am. Chem. Soc., 1989, 111, 8533– 8534; (b) T. Kato and J. M. J. Fréchet, Macromolecules, 1989, 22, 3818–3819.
- 12 M.-J. Brienne, J. Gabard, J.-M. Lehn and I. Stibor, J. Chem. Soc., Chem. Commun., 1989, 1868–1870.
- 13 (a) L. J. Yu, J. M. Wu and S. L. Wu, Mol. Cryst. Liq. Cryst., 1991, 198, 407–416; (b) L. J. Yu, Liq. Cryst., 1993, 14, 1303–1309.
- 14 C. M. Lee, C. P. Jarwala and A. C. Griffin, *Polymer*, 1994, 35, 4550– 4544.
- 15 (a) D. J. Price, H. Adams and D. W. Bruce, *Mol. Cryst. Liq. Cryst.*, 1996, 289, 127–140; (b) K. Willis, J. E. Luckhurst, D. J. Price, J. M. J. Fréchet, H. Kihara, T. Kato, G. Ungar and D. W. Bruce, *Liq. Cryst.*, 1996, 21, 585–587; (c) J. L. Nguyen, P. N. Horton, M. B. Hursthouse, A. C. Legon and D. W. Bruce, *J. Am. Chem. Soc.*, 2004, 126, 16–17.
- 16 (a) H. Zheng, C. K. Lai and T. M. Swager, Chem. Mater., 1994, 6, 101-103; (b) C. Paleos and P. Tsiourvas, Angew. Chem., Int. Ed. Engl., 1995, 34, 1696-1711; (c) R. Kleppinger, C. P. Lillya and C. Yang, J. Am. Chem. Soc., 1997, 119, 4097-4102; (d) M. Suárez, J.-M. Lehn, S. C. Zimmerman, A. Skoulios and B. Heinrich, J. Am. Chem. Soc., 1998, 120, 9526-9532; (e) K. Kanie, T. Yasuda, S. Ujiie and T. Kato, Chem. Commun., 2000, 1899-1900; (f) H. K. Lee, H. Lee, H. K. Young, Y. J. Chang, N.-K. Oh, W.-C. Zin and K. Kim, Angew. Chem., Int. Ed., 2001, 40, 2669-2671; (g) V. Percec, M. Glodde, T. K. Bera, Y. Miura, I. Shiyanovskaya, K. D. Singer, V. S. K. Balagurusamy, P. A. Heuney, I. Schnell, A. Rapp, N.-W. Spiess, S. D. Hudson and H. Duan, Nature, 2002, 419, 384-387; (h) R. I. Gearba, M. Lehmann, J. Levin, D. A. Ivanov, M. H. J. Koch, J. Barbera, M. G. Debije, J. Piris and Y. H. Geerts, Adv. Mater., 2003, 15, 1614-1618; (i) D. Goldmann, D. Janietz, C. Schmidt and J. H. Wendorff, J. Mater. Chem., 2004, 14, 1521-1525; (j) A. Kohlmeier, A. Nordsieck and D. Janietz, Chem. Mater., 2009 21 491-498
- 17 (a) J. Malthête, A. M. Levelut and H. T. Nguyen, J. Phys. Lett., 1985, 46, L875–L880; (b) H. T. Nguyen, C. Destrade, A.-M. Levelut and J. Malthête, J. Phys. (Paris), 1986, 47, 553–557; (c) J. Malthête, H. T. Nguyen and C. Destrade, Liq. Cryst., 1993, 13, 171–187; (d) R. P. Tuffin, K. J. Toyne and J. W. Goodby, J. Mater. Chem., 1996, 6, 1271–1282; (e) H.-T. Nguyen, C. Destrade and J. Malthête, Adv. Mater., 1997, 9, 375–388; (f) B. P. Hoag and D. L. Gin, Adv. Mater., 1998, 10, 1546–1551; (g) L. Plasseraud, L. G. Cuervo, D. Guillon, G. Süss-Fink, R. Deschenaux, D. W. Bruce and

B. Donnio, J. Mater. Chem., 2002, **12**, 2653–2658; (h) T. Yasuda, K. Kishimoto and T. Kato, Chem. Commun., 2006, 3399–3401.

- 18 (a) C. Tschierske, J. Mater. Chem., 2001, 11, 2647–2671; (b) X. Cheng, M. Prehm, M. K. Das, J. Kain, U. Baumeister, S. Diele, D. Leine, A. Blume and C. Tschierske, J. Am. Chem. Soc., 2003, 125, 10977– 10996.
- 19 M. Lee, B.-K. Cho, Y.-G. Jang and W.-C. Zin, J. Am. Chem. Soc., 2000, 122, 7449–7455.
- 20 Benzoic acid dimers: (a) A. E. Bradfield and B. Jones, J. Chem. Soc., 1929, 2660–2661; (b) G. W. Gray and B. Jones, J. Chem. Soc., 1953, 4179–4180.
- 21 Naphthoic acid dimers: (a) G. W. Gray and B. Jones, J. Chem. Soc., 1954, 683–686; (b) G. W. Gray and B. Jones, J. Chem. Soc., 1955, 236– 244.
- 22 Cinnamic acid dimers: G. M. Bennett and B. Jones, J. Chem. Soc., 1939, 420-425.
- Recent papers: (a) S. Kutsumizu, T. Ichikawa, M. Yamada, S. Nojima and S. Yano, J. Phys. Chem. B, 2000, 104, 10196–10205; (b) S. K. Kang and E. T. Samulski, Liq. Cryst., 2000, 27, 371–376; (c) K. U. Jeong, S. Jin, J. J. Ge, B. S. Knapp, J. Graham, J. Ruan, M. Guo, H. Xiong, F. W. Harris and S. Z. D. Cheng, Chem. Mater., 2005, 17, 2852–2865; (d) C. Lavigueur, E. J. Foster and V. E. Williams, J. Am. Chem. Soc., 2008, 130, 11791–11800; (e) X. Zhu, A. Mourran, U. Beginn, M. Moller, D. V. Anokhin and D. A. Ivanov, Phys. Chem. Chem. Phys., 2010, 12, 1444–1452.
- 24 (a) J. Tsibouklis, C. Campbell, A. R. Werninck, A. J. Shand and G. H. W. Milburn, *Polym. Bull.*, 1992, 29, 661–668; (b) T. Tanaka, Y. Honda, T. Tani, A. Terahara, Y. Tabe and M. Sugi, *Jpn. J. Appl. Phys.*, 1994, 33, 295–301; (c) A. L. Litvin, L. A. Samuelson, D. H. Charych, W. Spevak and D. L. Kaplan, *J. Phys. Chem.*, 1995, 99, 492–495; (d) P. T. Hammond and M. F. Rubner, *Macromolecules*, 1995, 28, 795–805; (e) T. Okuno, A. Izuoka, T. Ito, S. Kubo, T. Sugawara, N. Sato and Y. Sugawara, *J. Chem. Soc., Perkin Trans. 2*, 1998, 889–895; (f) J. Y. Chang, J. R. Yeon, Y. S. Shin, M. J. Han and S.-K. Hong, *Mater. Chem.*, 2000, 12, 1076–1082; (g) S. Kumar and S. K. Vaeshney, *Org. Lett.*, 2002, 4, 157–159; (h) H. J. Cho, K. Seo, C. J. Lee, H. Yun and J. Y. Chang, *J. Mater. Chem.*, 2003, 13, 986–990; (i) J. F. Nieremgarten, *Helv. Chim. Acta*, 2004, 87, 1357–1367.
- 25 B. G. Kim, S. Kim, J. Seo, N.-K. Oh, W.-C. Zin and S. Y. Park, *Chem. Commun.*, 2003, 2306–2307.
- 26 S. Dei, T. Shimogaki and A. Matsumoto, Synth. Met., 2009, 159, 969– 972.
- 27 L. Brandsma, *Preparative Acetylenic Chemistry*, Elsevier, Amsterdam, 2nd edn, 1988, pp. 212–214.
- 28 (a) K. Ohta, H. Muroki, K. Hatada, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1985, **130**, 249–263; (b) K. Ohta, H. Ema, H. Muroki, I. Yamamoto and K. Matsuzaki, *Mol. Cryst. Liq. Cryst.*, 1987, **147**, 61–78.
- 29 (a) A. M. Giroud-Godquin and J. Billard, Mol. Cryst. Liq. Cryst., 1981, 64, 147–150; (b) K. Ohta, H. Muroki, A. Takagi, I. Hatada, H. Ema, I. Yamamoto and K. Matsuzaki, Mol. Cryst. Liq. Cryst., 1986, 140, 131–152; (c) H. Sakashita, A. Nishitani, Y. Sumiya, H. Terauchi, K. Ohta and I. Yamamoto, Mol. Cryst. Liq. Cryst., 1988, 163, 211–219; (d) A. C. Ribeiro, A. F. Martin and A. M. Giroud-Godquin, Mol. Cryst. Liq. Cryst., Lett. Sect., 1988, 5, 133–139.
- 30 (a) S. Dei, T. Shimogaki and A. Matsumoto, *Macromolecules*, 2008,
   41, 6055–6065; (b) S. Dei and A. Matsumoto, *Macromol. Chem. Phys.*, 2009, 210, 11–20; (c) T. Shimogaki and A. Matsumoto, *Macromolecules*, 2011, 44, 3323–3327.
- 31 V. Enkelmann, Adv. Polym. Sci., 1984, 63, 91-136.
- 32 B. Tieke, Adv. Polym. Sci., 1985, 71, 79-151.
- 33 (a) V. Busico, A. Ferraro and M. Vacatello, J. Phys. Chem., 1984, 88, 4055–4058; (b) V. Busico, A. Ferraro and M. Vacatello, Mol. Cryst. Liq. Cryst., 1985, 128, 243–261.