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Flying-seed-like liquid crystals 3: new guideline for the induction of mesomorphism by using bulky groups instead of long alkyl chains†‡

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In our previous work, we synthesized a series of phthalocyanine-based flying-seed-like compounds, **(nPh-PhO)$_4$PcCu** (n = 3, 2, 1 and 0 in **nPh-PhO**: **a–d**), and revealed that each of them shows a columnar liquid crystalline phase (Col$_{ho}$ or Col$_{rho}$) from rt to an extremely high temperature near 500 °C. Thus, we could obtain columnar liquid crystalline phases for discotic compounds by using bulky substituents (**a–d**) instead of long alkyl chains. In order to further study the utility of these bulky substituents (**a–d**) on the induction of mesomorphism for other shaped molecules, we have synthesized novel flying-seed-like calamitic phenoxybenzoic acid derivatives, **nPh-PhOBA** (**3a–d**), and their Mitsubishi-Mark-shaped terbium complexes, **(nPh-PhOBA)$_3$Tb·mMeOH** (**4a–d**), in this work. Very interestingly, the mesomorphism of the phenoxybenzoic aids derivatives **nPh-PhOBA** (n = 0–3) was induced to show a mesophase (M$_x$) only by the bulky substituent **d** (n = 0), whereas the mesomorphism of their corresponding terbium complexes **(nPh-PhOBA)$_3$Tb(III)** (n = 0–3) was induced to show rectangular columnar (Col$_r$) mesophases by the bulky substituents **c** and **d** (n = 1, 0). On the other hand, the mesomorphism of the PcCu complexes **(nPh-PhOBA)$_4$PcCu** (n = 0–3) in our previous work was induced by all the bulky substituents **a**, **b**, **c** and **d** (n = 0–3). Thus, it becomes apparent that both calamitic and columnar mesomorphism can be induced by the substitution of bulky groups instead of long alkyl chains, and that the balance of the core size and the bulkiness of the substituents is very important to obtain mesomorphism in flying-seed-like compounds. We believe that this is a new guideline for the induction of mesomorphism by using bulky groups instead of long alkyl chains.

1 Introduction

It is well-known that molecular shapes of most liquid crystals are rod-like (calamitic) or disk-like (discotic). Furthermore, both molecular structures commonly have a rigid flat core and flexible long chains in the periphery. When such shapes of compounds are heated, the flexible long chains melt at first and the rigid flat cores do not melt, but still aggregate each other. This pre-melting of the peripheral long chains initiates the soft part to induce liquid-crystalline phases (mesophases). Hence, it is generally believed that the appearance of mesomorphism should require both a rigid flat core and long flexible chains in a molecule. However, in about 101 000 of the liquid crystals known to date, it has been reported that a very few liquid crystalline compounds are outside of this general criterion and they have neither a rigid flat core, nor long flexible chains in their molecules.[1–9]

In 1910, Vorländer reported the that alkali metal carboxylates, **Ph$_2$AcONa**, **(CH$_3$)$_2$AcOK** and **(C$_2$H$_5$)$_2$AcOK**, shown in Fig. 1 exhibit liquid crystalline phases, although they have neither a flat core nor long chains.[1] However, these interesting liquid crystals have been forgotten for about 100 years. It may be attributable to very high liquid crystalline temperature regions and their molecular structures being totally different from general calamitic and discotic liquid crystals.

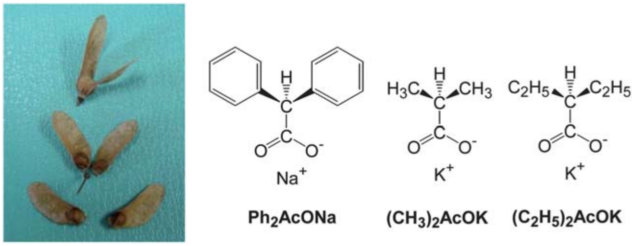

Fig. 1 Photograph of maple seeds and examples of flying-seed-like liquid crystals: ref. 1–4 and 6.

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† Part 2: ref. 12 in this paper.

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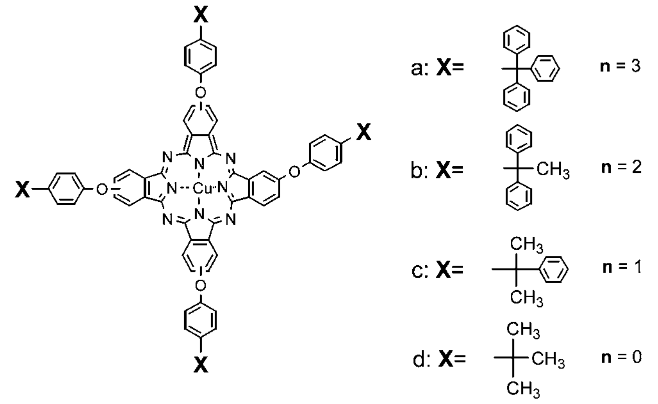
In 2006, we revealed, by using a temperature-dependent X-ray diffraction technique that **Ph_2AcONa** shows a hexagonal columnar (Col_h) mesophase, and **$(CH_3)_2AcOK$** and **$(C_2H_5)_2AcOK$** show a calamitic mesophase of the smectic A (S_A) phase.[6] Nevertheless, it was surprising to us that they have no long chains necessary for the formation of soft parts in the liquid crystalline phase. Therefore, we thought that the bulky substituents of the **Ph_2**-, **$(CH_3)_2$**- and **$(C_2H_5)_2$**-groups might form soft parts by free rotation, as in the flying-seeds shown in the photograph of maple seeds in Fig. 1. Accordingly, we named this type of liquid crystals as "flying-seed-like liquid crystals".[6] They are totally different from conventional calamitic and discotic liquid crystalline compounds.

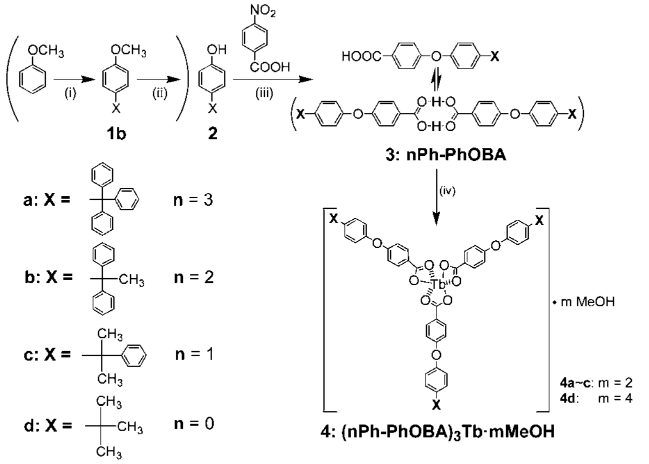
In 2004 and 2009, Usol'tseva and her co-workers reported that a phthalocyanine (Pc) compound **$(3Ph\text{-}PhO)_4PcCu$** exhibits a Col_h mesophase.[10,11] Although it has a rigid flat core, it has no long alkyl chains but the bulky triphenylmethylphenoxy groups (**a** in Fig. 2) in the periphery. The present bulky triphenylmethy-l-phenoxy group (**a**) closely resembles the **Ph_2**-group in a previous flying-seed-like liquid crystal **Ph_2AcONa** mentioned above (Fig. 1). Hence, we considered that this Pc compound **$(3Ph\text{-}PhO)_4PcCu$** was one of the flying-seed-like liquid crystals, and that the bulky triphenylmethylphenoxy groups (**a**) also formed soft parts in the mesophase. To certify this idea, we have synthesized four phthalocyanine-based flying-seed-like compounds, **(*n*Ph-PhO)$_4$PcCu** (n = 3–0), by using a series of bulky substituents (**a–d** in Fig. 2). Very interestingly, each of them shows a columnar liquid crystalline phase (Col_{ho} or Col_{rho}) from rt to an extremely high temperature, near 500 °C.[12] Thus, it was shown that columnar liquid crystalline phases can be induced for discotic compounds also by using bulky substituents (**a–d** in Fig. 2) instead of long alkyl chains.

We wished to further study the utility of these bulky substituents (**a–d** in Fig. 2) on the induction of mesomorphism for the other shaped molecules, such that in this work we have synthesized novel flying-seed-like calamitic phenoxybenzoic acid derivatives, ***n*Ph-PhOBA** (**3a–d** in Scheme 1), and their Mitsubish-Mark-shaped[13] terbium complexes, **(*n*Ph-PhOBA)$_3$Tb·*m*MeOH** (**4a–d** in Scheme 1), to investigate their mesomorphism.



(nPh-PhO)$_4$PcCu

Fig. 2 Molecular formula of phthalocyanine-based flying-seed-like liquid crystals, **(*n*Ph-PhO)$_4$PcCu**, in our previous work: ref. 10–12.



Scheme 1 Synthetic route for novel flying-seed-like calamitic ***n*Ph-PhOBA** (**3a–d**) and Mitsubishi-Mark-shaped **(*n*Ph-PhOBA)$_3$Tb·*m*MeOH** (**4a–d**) liquid crystals. (i) X–OH, polyphosphoric acid; (ii) 48% HBr aq. sol./HOAc; (iii) (1) K_2CO_3/DMF/*p*-nitrobenzoic acid (2) H^+, (iv) $(NO_3)_3Tb\cdot 6H_2O$–MeOH–ethylene glycol–NaOH for **4a**, **b**; $(NO_3)_3Tb\cdot 6H_2O$–MeOH–NaOH for **4c**, **d**.

2 Experimental

2.1 Synthesis

Scheme 1 shows the synthetic route for the present flying-seed-like calamitic ***n*Ph-PhOBA** (**3a–d**) compounds and the Mitsubishi-Mark-shaped **(*n*Ph-PhOBA)$_3$Tb·*m*MeOH** (**4a–d**) complexes. The starting materials, phenol derivatives **2a**, **c** and **d**, were purchased from Tokyo Chemical Industry, and they were used without further purification. Since the phenol derivative **2b** was not commercially available, it was prepared as shown in this scheme. Commercially available anisole was reacted with 1,1-diphenylethanol to obtain 4-[1,1-diphenylethoxy]anisole **1b**, and then it was demethylated with hydrobromic acid by using the method of Evangelista *et al.*[14] to afford the phenol derivative **2b**. The phenol derivatives **2a–d** were reacted with *p*-nitrobenzoic acid to obtain the corresponding 4-[4-(bulky-group-substituted)phenoxy]benzoic acids, ***n*Ph-PhOBA** (**3a–d**). The phenoxybenzoic acids **3a–d** were metalated with terbium(III) nitrate hexahydrate under basic conditions to afford the solvated derivatives **(*n*Ph-PhOBA)$_3$Tb·*m*MeOH** (**4a–d**).

The detailed procedures are described only for the representative derivatives, **2b**, **3a**, **4a** and **4c**. Almost the same procedures for **3b**, **3c** and **3d** are described in the ESI file.‡

4-(1,1-Diphenylethyl)phenol (2b). Into a 200 ml three-necked flask, anisole (1.1 g, 10 mmol), 1,1-diphenylethanol (2.0 g, 10 mmol) and polyphosphoric acid (20 g, 200 mmol) were poured. It was heated with stirring at 100 °C for 23 hours. After cooling to rt, the reaction mixture was extracted with diethyl ether and washed with NaCl saturated aqueous solution. The organic layer was dried over sodium sulfate and the evaporated *in vacuo*. Into a 100 ml three-necked flask, 2.5 g of the residue, 58 ml of glacial acetic acid and 14.5 ml of 48% hydrobromic acid aqueous solution were poured. It was heated with stirring at 100 °C for 16 hours. After cooling to rt, the reaction mixture was extracted with $CHCl_3$ and washed with NaCl saturated aqueous solution. The organic layer was dried over sodium sulfate and then dried *in vacuo*. The residue was purified by column chromatography (120 g of silica gel, CH_2Cl_2, $R_f = 0.33$) to afford 0.68 g of an ocherous solid, obtained in a 25% yield.

IR (KBr): 3487 (Ar–OH) cm^{-1}.

^{1}H-NMR (DMSO-d_6: TMS) δ 2.32 (3H, s, –CH_3), 7.02–7.24 (14H, m, aromatic –*H*), 9.44 (1H, s, O–*H*).

4-(4-Tritylphenoxy)benzoic acid (3a). A 100 ml three-necked flask with a condenser was dried by a heat gun under a nitrogen atmosphere. Into this flask, *p*-nitrobenzoic acid (0.18 g, 1.1 mmol), freshly distilled dry DMF (5 ml), K_2CO_3 (0.35 g, 2.5 mmol), and 4-triphenylmethylphenol (**2a**: 0.44 g, 1.3 mmol) were poured. It was heated with stirring under a dry nitrogen atmosphere at 110 °C for 6 hours. After cooling to rt, it was neutralised by adding 10% hydrochloric acid dilute aqueous solution, and then extracted with diethyl ether and washed with NaCl saturated aqueous solution. The organic layer was dried over sodium sulfate and dried *in vacuo*. The residue was recrystallised from ethanol to afford 0.33 g of a white solid in a 67% yield. M.p.: see Table 2.

IR (KBr): 3489 (–OH), 1710 (C=O), 1280 (ether) cm^{-1}.

^{1}H-NMR (DMSO-d_6: TMS) δ 6.66 (2H, d, $J = 9.1$ Hz, aromatic –*H*), 6.93 (2H, d, $J = 9.0$ Hz, aromatic –*H*), 7.08–7.32 (19H, m, aromatic –*H*), 9.36 (1H, s, COO–*H*).

$(3Ph\text{-}PhOBA)_3Tb\cdot 2MeOH$ (4a). Into a 50 ml Erlenmeyer flask, NaOH (0.048 g, 1.2 mmol), terbium(III) nitrate hexahydrate (0.14 g, 0.30 mmol), 4-(4-tritylphenoxy) benzoic acid (**3a**: 0.46 g, 1.0 mmol), MeOH (5 ml) and ethylene glycol (0.5 ml) were added, and it was stirred at rt for 24 hours. The resulting precipitate was collected by filtration and washed with MeOH. The residue was dried *in vacuo* to afford 0.31 g of white crystals in a 60% yield.

$(2Ph\text{-}PhOBA)_3Tb\cdot 2MeOH$ (4b). In the same manner as **4a**, it could be prepared to afford 0.30 g of white crystals in a 65% yield.

$(1Ph\text{-}PhOBA)_3Tb\cdot 2MeOH$ (4c). Into a 50 ml Erlenmeyer flask, NaOH (0.048 g, 1.2 mmol), terbium(III) nitrate hexahydrate (0.14 g, 0.30 mmol), 4-[4-(1-methyl-1-phenylethyl) phenoxy] benzoic acid (**3c**: 0.33 g, 1.0 mmol) and MeOH (5 ml) were added, and it was stirred at rt for 24 hours. The resulting precipitate was collected by filtration and washed with MeOH. The residue was dried *in vacuo* to afford 0.25 g of white crystals in a 64% yield.

$(0Ph\text{-}PhOBA)_3Tb\cdot 4MeOH$ (4d). In the same manner as **4c**, it could be prepared to afford 0.20 g of white crystals in a 55% yield.

2.2 Measurements

The compounds synthesized here were identified by using FT-IR (Nicolet NEXUS670 FT-IR), ^{1}H-NMR (Bruker DRX-400), elemental analysis (Perkin-Elmer elemental analyzer 2400), and thermal gravimetric analysis (Rigaku Thermo plus TG8120). The phase transition behaviour of the present compounds (**3a–d** and **4a–d**) was observed with a polarizing optical microscope (Nikon ECLIPSE E600 POL) equipped with a Mettler FP82HT hot stage and a Mettler FP-90 Central Processor, and a Shimadzu DSC-50 differential scanning calorimeter. For the mesophase identification, we employed a new small angle X-ray diffractometer (Bruker Mac SAXS System) equipped with a temperature-variable sample holder adapted Mettler FP82HT hot stage. Fig. S1 and S2‡ illustrate the setup of the SAXS system and the setup of the temperature-variable sample holder, respectively. As can be seen from Fig. S1,‡ the generated X-ray is bent by two convergence monochrometers to produce a point X-ray beam (diameter = 1.0 mm). The point beam runs through holes of the temperature-variable sample holder. As is illustrated in Fig. S2,‡ into the temperature-variable sample holder of the Mettler FP82HT hot stage, a glass plate (76 mm × 19 mm × 1.0 mm) having a hole (diameter = 1.5 mm) is inserted. The hole can be charged with a powder sample (*ca.* 1 mg). The measurable range is from 3.0 Å to 100 Å and the temperature range is from rt to 375 °C. This SAXS system enabled us to greatly reduce the amount of samples. The measurement time only needed 60–300 seconds, which was efficient to suppress the sample decomposition. Temperature-dependent fluorescence spectra of **4c**, **d** were recorded using a Horiba Fluorolog FL3-21-NIR-OS spectrofluorometer equipped with a handmade hot plate[15] available from rt to 400 °C with a temperature controller.

3 Results and discussion

3.1 Synthesis

As can be seen from Scheme 1, the fourth synthetic step (iv) from the phenoxybenzoic acid derivatives to the terbium complexes was successful for **4c** and **d** by using a single reaction solvent, MeOH. On the other hand, it was not successful for **4a** and **b** by using the single solvent MeOH. This was attributable to the low solubilities of **3a** and **b** in pure MeOH, which resulted from the large number of phenyl groups in the bulky substituents. When a mixture solvent of MeOH and ethylene glycol (10 : 1 v/v) was adopted for **3a** and **b**, the metallation successfully took place, to afford the terbium complexes **4a**, and **b**.

As can be seen from the elemental analysis data in Table 1, each of the terbium complexes **4a–c** contained two MeOH molecules as the crystal solvent in the freshly prepared (virgin) sample. On the other hand, the terbium complex **4d** contained four MeOH molecules as the crystal solvent. The number of MeOH molecules (*m* in Scheme 1) could be also confirmed from the thermal gravimetric analysis (TGA) as shown in Fig. 3. As can be seen from the DSC thermograms in this figure, each of the virgin samples (the first heating runs) of **4c** and **d** gave a large endothermic peak with an onset at *ca.* 50 °C, whereas it disappeared in the second heating runs. As can be seen from the TGA thermograms in this figure, the virgin samples of **4c** and **4d** gave 5.1% and 11.9% of weight losses at *ca.* 50 °C, respectively. The weight losses of **4c** and **4d** exactly correspond to the weights of two and four MeOH molecules, respectively. It is consistent with the elemental analysis data in Table 1 mentioned above. The terbium complex **4d** only contains four MeOH molecules. It may be attributed to more space around the Mitsubishi-Mark-shaped terbium complex **4d** ($n = 0$) in comparison with the other bulky phenyl-group-substituted terbium complexes **4a–c** ($n = 3–1$).

Table 1 Elemental analysis data of **(*n*Ph-PhOBA)3Tb·*m*MeOH**, **4a–d**

Compound	Molecular formula	Elemental analysis: found (calcd)/% C	H	N
4a: (3Ph-PhOBA)$_3$Tb·2MeOH	$C_{98}H_{77}O_{11}Tb$	73.83 (74.05)	4.85 (4.88)	0.02 (0.00)
4b: (2Ph-PhOBA)$_3$Tb·2MeOH	$C_{83}H_{71}O_{11}Tb$	70.94 (71.04)	5.02 (5.10)	0.01 (0.00)
4c: (1Ph-PhOBA)$_3$Tb·2MeOH	$C_{68}H_{65}O_{9}Tb$	66.85 (67.10)	5.21 (5.38)	0.10 (0.00)
4d: (0Ph-PhOBA)$_3$Tb·4MeOH	$C_{55}H_{67}O_{13}Tb$	62.07 (62.14)	6.43 (6.35)	0.01 (0.00)

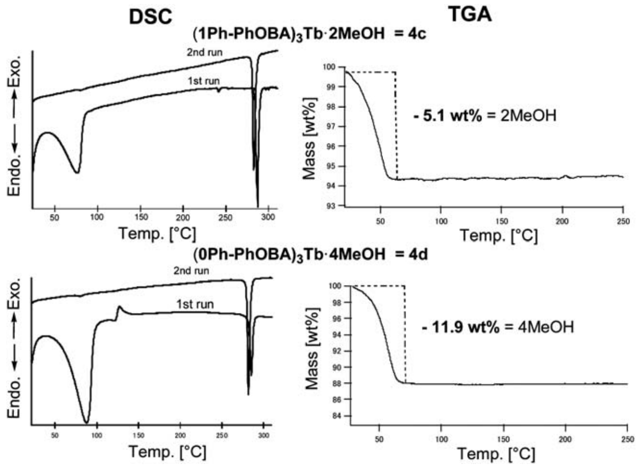


Fig. 3 DSC and TGA thermograms of **(1Ph-PhOBA)$_3$Tb·2MeOH** (**4c**) and **(0Ph-PhOBA)$_3$Tb·4MeOH** (**4d**).

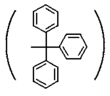
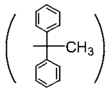
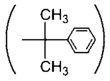
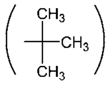
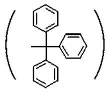
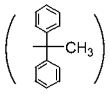
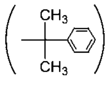
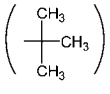
3.2 Mesomorphic properties

The phase transition sequences for the flying-seed-like calamitic phenoxybenzoic acid derivatives ***n*Ph-PhOBA** (**3a–d**) and their corresponding desolventized Mitsubishi-Mark-shaped terbium complexes **(*n*Ph-PhOBA)$_3$Tb** (**3a–d**) are summarized in Table 2.

Mesomorphism of 0Ph-PhOBA (3d). It is well known and established that long alkyl-chain-substituted benzoic acid derivatives form dimers by hydrogen bonding and show mesomorphism.[16–18] The present phenoxybenzoic acid derivatives ***n*Ph-PhOBA** (**3a–d**) may also form dimers as illustrated in Scheme 1.

As can be seen from Table 2, the phenoxybenzoic acid derivatives **3a–c** are not liquid-crystalline but crystalline. On the other hand, the derivative **3d** is only liquid-crystalline. All the compounds **3** are so sublime at high temperatures especially after the clearing point that no samples were in the DSC cell and gave no DSC peaks on the 1st cooling and the 2nd heating runs (Table 2). Since the derivative **3d** is so sublime at high temperatures, it was very difficult to observe the liquid-crystalline texture by a polarizing microscope (POM). When this derivative was gradually heated from rt, it completely sublimated and disappeared before reaching the mesophase temperature range. Therefore, the sample was inserted into the hot stage pre-heated at a certain temperature under the clearing point (cp) of 246 °C. The set temperature was lowered gradually from the cp and observed by the POM step by step. Eventually, we could observe the liquid-crystalline texture at 220 °C as shown in the photomicrograph in Fig. 4. As can be seen from this photomicrograph, the crystalline phase K was changing into a marble texture with fluidity characteristics to a nematic phase.[19] However, it rapidly sublimed within one minute so that the mesophase could not be identified unambiguously. Hence,

Table 2 Phase transition sequences for the flying-seed-like calamitic ***n*Ph-PhOBA** (**3a–d**), and desolventized Mitsubishi-Mark-shaped **(*n*Ph-PhOBA)$_3$Tb** (**4a–d**) liquid crystals[a]

Compound		Phase[b]	$\xrightarrow{T(°\mathrm{C})[\Delta H(\mathrm{kJ\ mol^{-1}})]}$			Phase
3a		K	$\xrightarrow{288[73.0]}$			I. L. (Subl.)
3b		K	$\xrightarrow{176[94.7]}$			I. L. (Subl.)
3c		K	$\xrightarrow{193[94.8]}$			I. L. (Subl.)
3d		K	$\overbrace{\xrightarrow{220^*} M_x \xrightarrow{246}}^{[167]}$			I. L. (Subl.)
4a		K	$\xrightarrow{356}$			dc
4b		K	$\xrightarrow{334}$			dc
4c		K	$\xrightarrow{286[44.1]}$	$\mathrm{Col_r}$ $P2_1/a$	$\xrightarrow{314}$	dc
4d		K	$\xrightarrow{282[35.5]}$	$\mathrm{Col_r}$ $P2m$	$\xrightarrow{308}$	dc

[a] All the phase transition temperatures with enthalpy changes were determined with DSC for the 1st heating run, except for the asterisk-marked temperature which was observed only with POM. The decomposition temperatures were determined with TGA as the onset temperatures. [b] Phase nomenclature: K = crystal, M_x = unidentified mesophase, $\mathrm{Col_r}$ = rectangular columnar mesophase, I. L. (Subl.) = isotropic liquid (accompanied by vigorous sublimation) and dc = decomposition.

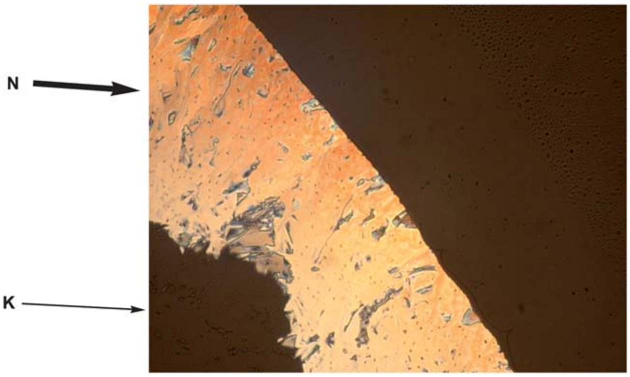


Fig. 4 Photomicrograph of **0Ph-PhOBA** (**3d**) at 220 °C. The crystalline phase K was changing into an unidentified mesophase (M_x) showing a marble texture.

this mesophase was denoted as an unidentified mesophase (M_x). Nevertheless, this means that we can also obtain calamitic liquid crystals substituted by bulky groups instead of long alkyl chains. The present phenoxybenzoic acid derivative **3d** is the first example of flying-seed-like calamitic liquid crystal, so far as we know.

As can be seen from Table 2, the enthalpy of 167 kJ mol^{-1} between 220* and 246 °C of **3d** seems to be too large even for the combined enthalpies of melting (K-M_x) and clearing (M_x-I. L.) in comparison with general mesogenic compounds. Although it is not clear at the present time, the sublimation enthalpy might be included. The compound **3d** gave the most vigorous sublimation nature among the compounds **3a–d**. Hence, it would give the biggest enthalpy among them.

As mentioned above, the bulky phenyl-group-substituted phenoxybenzoic acid derivatives **3a–c** are not liquid-crystalline. It may be attributable to too small a core in comparison with the bulkier substituents. Thus, these flying-seed-like compounds suggest that the balance of the core size and the bulkiness of the substituents is very important to obtain mesomorphism.

Mesomorphism of (nPh-PhOBA)$_3$Tb(III) (n = 1, 0: 4c and d). As can be seen from Table 2, the Mitsubishi-Mark-shaped terbium complexes **4a** and **4b** are not liquid-crystalline but crystalline until their very high decomposition temperatures. On the other hand, **4c** and **4d** exhibit a mesophase at very high temperatures. It is very interesting that the mesomorphism of the phenoxybenzoic aids derivatives ***n*Ph-PhOBA** (n = 0–3) was induced only by the bulky substituent **d** (n = 0), but that the mesomorphism of their corresponding terbium complexes **(nPh-PhOBA)$_3$Tb(III)** (n = 0–3) was induced by the bulky substituents **c** and **d** (n = 1, 0). On the other hand, the mesomorphism of the PcCu complexes **(nPh-PhOBA)$_4$PcCu** (n = 0–3) in our previous work was induced by all the bulky substituents **a**, **b**, **c** and **d** (n = 0–3).[12] Therefore, the balance of the core size and the bulkiness of the substituents is very important to obtain mesomorphism for flying-seed-like compounds.

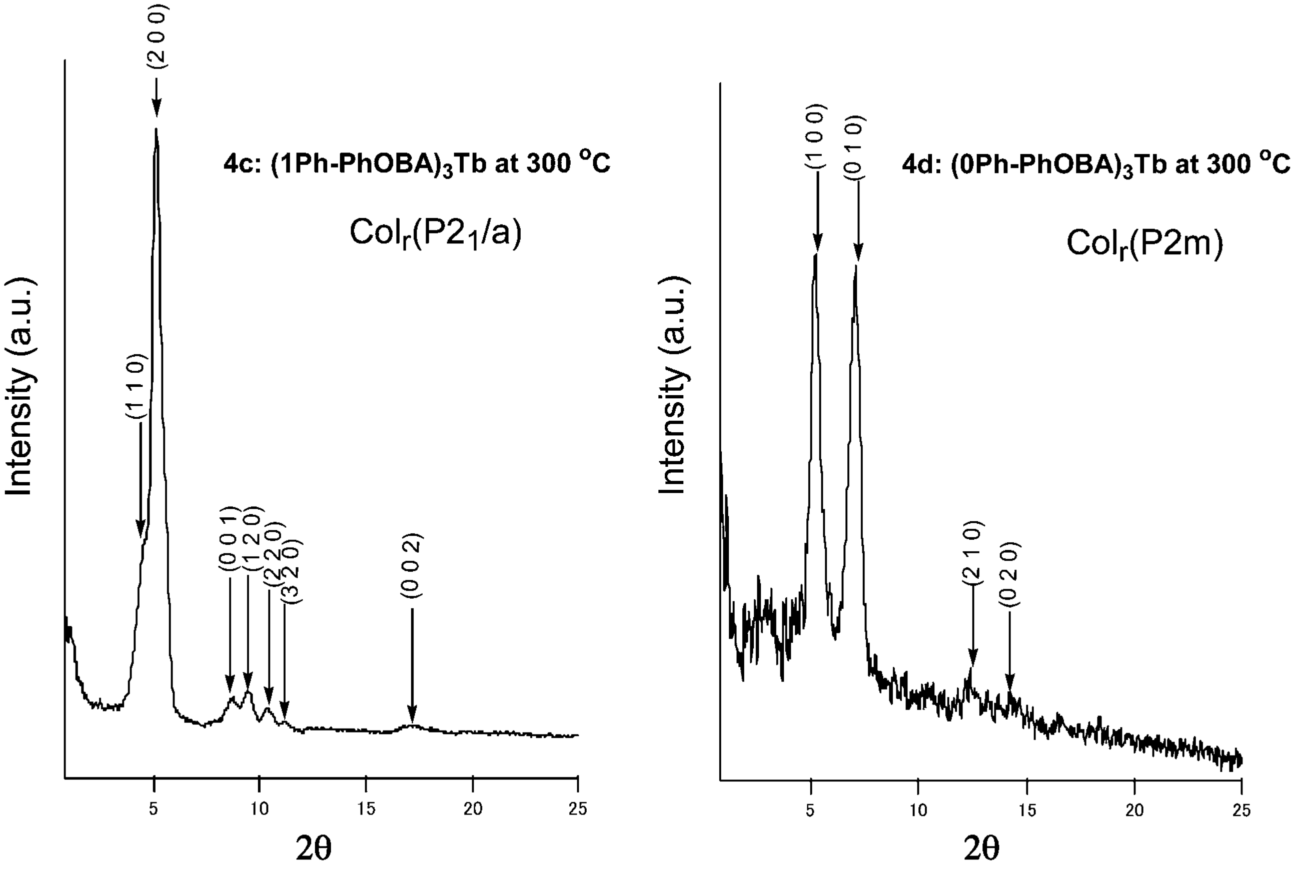


Fig. 5 X-ray diffraction patterns of **(1Ph-PhOBA)$_3$Tb** (**4c**) and **(0Ph-PhOBA)$_3$Tb** (**4d**) at 300 °C.

Fig. 5 shows the X-ray diffraction patterns of **4c** and **4d** at 300 °C. The corresponding X-ray data are listed in Table 3. As can be seen from this table, the Mitsubishi-Mark-shaped terbium complexes **4c** and **4d** give rectangular columnar mesophases, $\mathrm{Col_r}(P2_1/a)$ and $\mathrm{Col_r}(P2m)$, respectively. The small symmetrical difference between them may originate from the difference in the bulkiness of the substituted groups of **c** and **d**. Interestingly, **$(1Ph\text{-}PhOBA)_3Tb$** (**4c**) showed two stacking distances of dimers and monomers at 10.1 and 5.14 Å, respectively. This means that an equilibrium between dimers and monomers exists in the columns. The Mitsubishi-Mark-shaped terbium complexes **4c** may form anti-parallel dimers in which one Mitsubishi-Mark stacks on another Mitsubishi-Mark rotated by 60 degree.

As mentioned above, the present terbium complexes **4c** and **4d** exhibit a mesophase at very high temperatures, which is characteristic to flying-seed-like liquid crystals.[12]

3.3 Temperature-dependent fluorescence spectra

The temperature-dependent fluorescence spectra of the thin films of **4c** and **4d** are shown in Fig. 6. In Fig. 7 are plotted the logarithm of the intensities at 545 nm *versus* temperature. As can be seen from these figures, the intensities decrease with increasing temperature.[20–22] A large deformation of the spectrum of **4c** at 300 °C corresponds to a considerable decomposition of the sample in air for the long measurement time. The decomposition temperature 314 °C listed in Table 2 was the measured value with TGA under a nitrogen atmosphere. The present temperature-dependent fluorescence spectral measurements were carried out in air for long time. Therefore, the decomposition in air started even at temperatures lower than the TGA decomposition temperatures, and progressed for a long time. Additionally, the colour of the sample measured at 300 °C changed from white to brown.

Although there have been several reports that the fluorescence intensities change with phase transitions,[20–23] the present terbium complexes did not show discernible drastic changes for their desolventizing and phase transitions, as can be seen from Fig. 7. Therefore, the fluorescence spectral changes of the present terbium complexes only depend on their thermal stability.

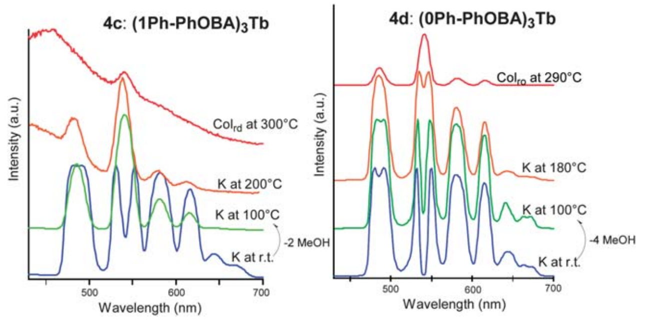


Fig. 6 Temperature-dependent fluorescence spectra of **$(1Ph\text{-}PhOBA)_3Tb\cdot 2MeOH$** (**4c**) and **$(0Ph\text{-}PhOBA)_3Tb\cdot 4MeOH$** (**4d**).

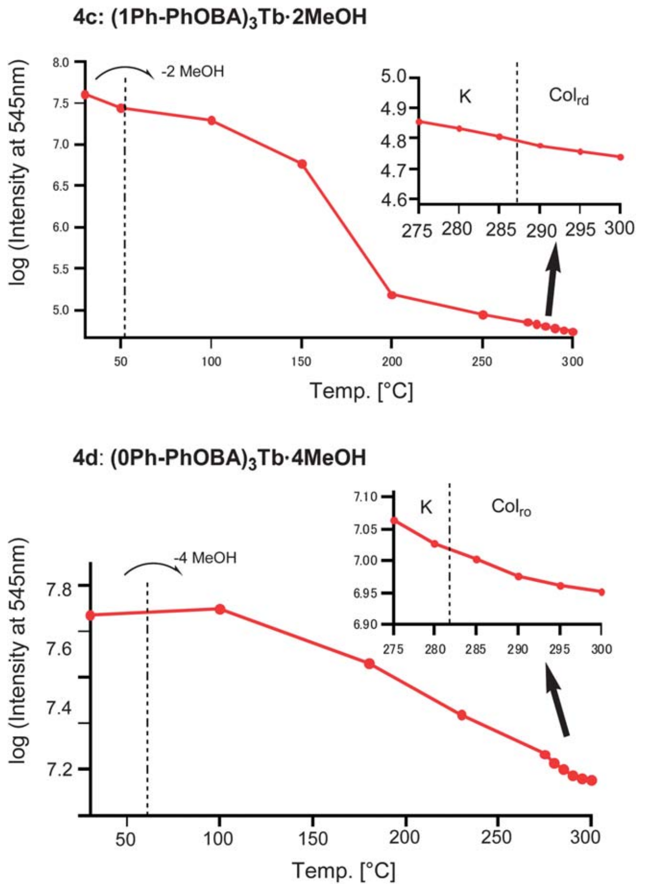


Fig. 7 Fluorescent intensities at 545 nm *versus* temperature for **$(1Ph\text{-}PhOBA)_3Tb\cdot 2MeOH$** (**4c**) and **$(0Ph\text{-}PhOBA)_3Tb\cdot 4MeOH$** (**4d**).

Table 3 X-ray data of **$(1Ph\text{-}PhOBA)_3Tb$** (**4c**) and **$(0Ph\text{-}PhOBA)_3Tb$** (**4d**)

Compound Mesophase	Spacing/Å Observed	Spacing/Å Calculated	Miller indices (h k l)
4c: $(1Ph\text{-}PhOBA)_3Tb$			
$\mathrm{Col_r}$ ($P2_1/a$) at 300 °C	19.6	19.6	(2 0 0)
a = 39.2 Å	17.3	17.3	(1 1 0)
b = 19.3 Å	10.1	10.1	(0 0 1)^a
c = 10.1 Å	9.37	9.36	(1 2 0)
Z = 4.0 for ρ = 1.00^c	8.53	8.64	(2 2 0)
	7.87	7.75	(3 2 0)
	5.14	5.07	(0 0 2)^b
4d: $(0Ph\text{-}PhOBA)_3Tb$			
$\mathrm{Col_r}$($P2m$) at 300 °C	16.9	16.9	(1 0 0)
a = 16.9 Å	12.5	12.5	(0 1 0)
b = 12.5 Å	7.14	6.99	(2 1 0)
	6.20	6.23	(0 2 0)

[a] Stacking distance between dimers. [b] Stacking distance between monomers. [c] Assumed value.

4 Conclusion

We have synthesized novel flying-seed-like calamitic phenoxybenzoic acid derivatives, ***n*Ph-PhOBA** (**3a–d**), and their Mitsubishi-Mark-shaped terbium complexes, **$(n\mathrm{Ph\text{-}PhOBA})_3\mathrm{Tb}\cdot m\mathrm{MeOH}$** (**4a–d**), and investigated their mesomorphism.

The phenoxybenzoic acid derivatives **3a–c** are not liquid-crystalline but crystalline, whereas the derivative **3d** is only liquid-crystalline. The derivative **3d** shows an unidentified mesophase (M_x) at very high temperatures from 220 °C to 246 °C. It is the first example of a flying-seed-like calamitic liquid crystal, as far as we know. On the other hand, the terbium complexes **4a** and **4b** are not liquid-crystalline but crystalline, whereas **4c** and **4d** exhibit the rectangular columnar mesophases $\mathrm{Col_r}(P2_1/a)$ and $\mathrm{Col_r}(P2m)$, respectively. It is very interesting that the PcCu complexes **(*n*Ph-PhOBA)$_4$PcCu** in our previous work are liquid crystalline for all the bulky substituents **a**, **b**, **c** and **d**.

Thus, it becomes apparent that both calamitic and columnar mesomorphism can be induced by bulky group substituents instead of long alkyl chains, and that the balance of the core size and the bulkiness of the substituents in flying-seed-like compounds is very important to obtain mesomorphism. We believe that this is a new guideline for induction of mesomorphism by using bulky groups instead of long alkyl chains.

References

1 D. Vorländer, *Ber. Dtsch. Chem. Ges.*, 1910, **43**, 3120–3125.

2 D. Demus, H. Sackmann and K. Seibert, *Wiss. Z. – Martin-Luther-Univ. Halle-Wittenberg, Math.-Naturwiss. Reihe*, 1970, **5**, 47–62.

3 P. Ferloni, M. Sanesi, P. L. Tonelli and P. Franzosini, *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.*, 1978, **33**, 240–242.

4 M. Sanesi, P. Ferloni, G. Spinolo and P. L. Tonelli, *Z. Naturforsch., A: Phys., Phys. Chem., Kosmophys.*, 1978, **33**, 386–388.

5 R. van Deun, J. Ramaekers, P. Nockemann, K. van Hecke, L. van Meervelt and K. Binnemans, *Eur. J. Inorg. Chem.*, 2005, 563–571.

6 K. Ohta, T. Shibuya and M. Ando, *J. Mater. Chem.*, 2006, **16**, 3635–3639.

7 S. Basurto, S. Garcia, A. G. Neo, T. Torroba, C. F. Marcos, D. Miguel, J. Barbera, M. B. Ros and M. R. de la Fuente, *Chem.–Eur. J.*, 2005, **11**, 5362–5376.

8 M. Shimizu, M. Nata, K. Watanabe, T. Hiyama and S. Ujiie, *Mol. Cryst. Liq. Cryst.*, 2005, **441**, 237–241.

9 M. Shimizu, M. Nata, K. Mochida, T. Hiyama, S. Ujiie, M. Yoshio and T. Kato, *Angew. Chem., Int. Ed.*, 2007, **46**, 3055–3058.

10 N. Usol'tseva, V. Bykova, G. Ananjeva, N. Zharnikova and E. Kudrik, *Mol. Cryst. Liq. Cryst.*, 2004, **411**, 1371–1378.

11 N. Zharnikova, N. Usol'tseva, E. Kudrik and M. Theakkat, *J. Mater. Chem.*, 2009, **19**, 3161–3167.

12 Y. Takagi, K. Ohta, S. Shimosugi, T. Fujii and E. Itoh, *J. Mater. Chem.*, 2012, **22**, 14418–14425.

13 Mitsubish-Mark: see http://www.mitsubishi.com/e/group/mark.html.

14 R. A. Evangelista, H. E. Wong, E. F. G. Templeton, T. Granger, B. Allore and A. Pollak, *Anal. Biochem.*, 1992, **203**, 218–226.

15 T. Shibuya, Appendix 1 in Master Thesis, Shinshu University, Ueda, 2006.

16 N. K. Lokanath, D. Krishne Gowda, D. Revannasiddaiah, M. M. M. Abdoh, M. A. Sridhar and J. Shashidhara Prasad, *Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A*, 1998, **317**, 153–164.

17 A. Sato, Y. Yanamura, K. Saito and M. Sorai, *Liq. Cryst.*, 1999, **26**, 1185–1195.

18 T. Shimogaki, S. Dei, K. Ohta and A. Matsumoto, *J. Mater. Chem.*, 2011, **21**, 10730–10737.

19 D. M. Small, M. C. Bourges and D. G. Dervichian, *Biochim. Biophys. Acta, Lipids Lipid Metab.*, 1966, **125**, 563–580.

20 E. Venuti, R. G. Della Valle, I. Bilotti, A. Brillante, M. Cavallini, A. Calò and Y. H. Geerts, *J. Phys. Chem. C*, 2011, **115**, 12150–12157.

21 C.-T. Liao, H.-H. Chen, H.-F. Hsu, A. Poloek, H.-H. Yeh, Y. Chi, K.-W. Wang, C.-H. Lai, G.-H. Lee, C.-W. Shih and P.-T. Chou, *Chem.–Eur. J.*, 2011, **17**, 546–556.

22 C. V. Yelamaggad, A. S. Achalkumar, D. S. S. Rao and S. K. Prasad, *J. Org. Chem.*, 2009, **74**, 3168–3171.

23 R. Cristian, J. Eccher, I. H. Bechtold, C. N. Tironi, A. A. Vieira, F. Molin and H. Gallardo, *Langmuir*, 2012, **28**, 11590–11598.