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Flying-seed-like liquid crystals **3**[†]: New guideline for 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**)₄PcCu (n = 3, 2, 1 and 0 in **nPh-PhO**: **a**, **b**, **c** and **d**), and revealed that each of them shows a columnar liquid crystalline phase (Col_{ho} or Col_{tho}) 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 furthermore study the utility of these bulky substituents (**a**~**d**) on induction of mesomorphism for the 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**)₃Tb·mMeOH (**4a**~**d**), in this work. Very interestingly, the mesomorphism of the phenoxybenzoic acids 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**)₃Tb(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**)₄PcCu(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 substitution of bulky groups instead of long alkyl chains, and that balance of core size and bulkiness of substituents is very important to obtain mesomorphism in flying-seed-like compounds. We believe that this is a new guideline for 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 of the molecular structures commonly have a rigid flat core and flexible long chains in the periphery. When such shape 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 peripheral long chains originates the soft part to induce liquid-crystalline phases (mesophases). Hence, it is generally believed that appearance of mesomorphism should require both a rigid flat core and long flexible chains in a molecule. However, in about 101,000 of liquid crystals known until now it has been reported that a very few liquid crystalline compounds are out of this general criterion and they have neither a rigid flat core nor long flexible chains in their molecules^{1)~9)}.

In 1911, Vorländer reported that alkali metal carboxylates, **Ph₂AcONa**, (**(CH₃)₂AcOK**) and (**(C₂H₅)₂AcOK**), shown in Fig.1 exhibit liquid crystalline phases, although they have neither a flat core nor long chains¹⁾. 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 totally different from general calamitic and discotic liquid crystals.

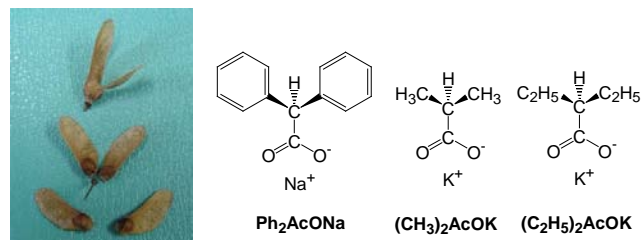


Fig. 1 Photograph of maple seeds and examples of flying-seed-like liquid crystals: Refs. 1~4 and 6.

In 2006 we revealed by using temperature-dependent X-ray diffraction technique that **Ph₂AcONa** shows a hexagonal columnar (Col_h) mesophase, and **(CH₃)₂AcOK** and **(C₂H₅)₂AcOK** show a calamitic mesophase of smectic A (S_A) phase⁶⁾. Nevertheless, it was surprising for us that they have no long chains necessary for formation of soft parts in liquid

crystalline phase. Therefore, we thought that these bulky substituents of Ph_2 -, $(\text{CH}_3)_2$ - and $(\text{C}_2\text{H}_5)_2$ -groups might form soft parts by free rotation, like as flying-seeds as 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.

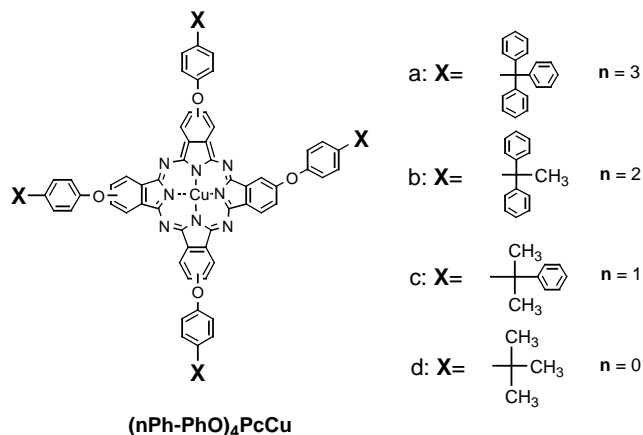


Fig. 2 Molecular formula of phthalocyanine-based flying-seed-like liquid crystals, $(\text{nPh-PhO})_4\text{PcCu}$, in our previous work: Refs.10~12.

In 2004 and 2009, Usol'tseva and her co-workers reported that a phthalocyanine (Pc) compound $(3\text{Ph-PhO})_4\text{PcCu}$ exhibits a Col_h mesophase^{10,11}. Although it has a rigid flat core, it has no long alkyl chains but bulky triphenylmethyl-phenoxy groups (**a** in Fig. 2) in the periphery. The present bulky triphenylmethyl-phenoxy group (**a**) very resembles Ph_2 -group in a previous flying-seed-like liquid crystal Ph_2AcONa mentioned above (Fig. 1). Hence, we considered that this Pc compound $(3\text{Ph-PhO})_4\text{PcCu}$ 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, $(\text{nPh-PhO})_4\text{PcCu}$ ($n=3\sim 0$), 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_{rbo}) from rt to an extremely high temperature near 500 °C¹². Thus, it was proved 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 wish to furthermore study the utility of these bulky substituents (**a-d** in Fig. 2) on induction of mesomorphism for the other shaped molecules, so that in this work we have synthesized novel flying-seed-like calamitic phenoxybenzoic acid derivatives, nPh-PhOBA (**3a-d** in Scheme 1), and their Mitsubishi-Mark-shaped¹³ terbium complexes, $(\text{nPh-PhOBA})_3\text{Tb}\cdot m\text{MeOH}$ (**4a-d** in Scheme 1), to investigate their mesomorphism.

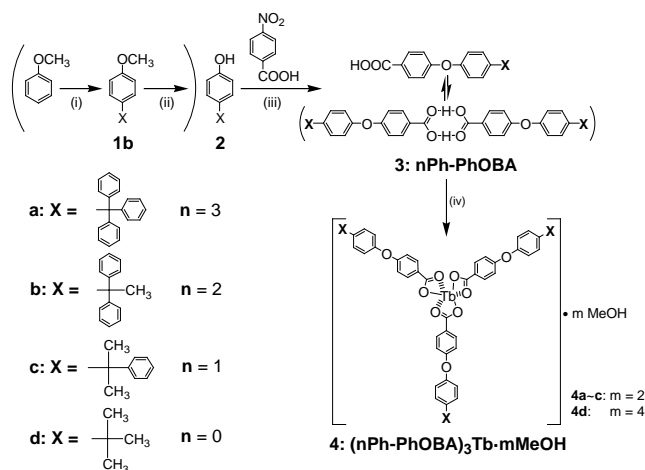
2. Experimental

2-1. Synthesis

Scheme 1 shows synthetic route for the present flying-seed-like calamitic nPh-PhOBA (**3a-d**) compounds and Mitsubishi-Mark-shaped $(\text{nPh-PhOBA})_3\text{Tb}\cdot m\text{MeOH}$ (**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, nPh-PhOBA (**3a-d**). The phenoxybenzoic acids **3a-d** were metalated with terbium(III) nitrate hexahydrate in basic condition to afford the solvated derivatives $(\text{nPh-PhOBA})_3\text{Tb}\cdot m\text{MeOH}$ (**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 supplementary information file.



Scheme 1 Synthetic route for novel flying-seed-like calamitic nPh-PhOBA (**3a~d**) and Mitsubishi-Mark-shaped $(\text{nPh-PhOBA})_3\text{Tb}\cdot m\text{MeOH}$ (**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) $(\text{NO}_3)_3\text{Tb}\cdot 6\text{H}_2\text{O}$ / MeOH / ethylene glycol / NaOH for **4a,b**; $(\text{NO}_3)_3\text{Tb}\cdot 6\text{H}_2\text{O}$ / MeOH / NaOH for **4c,d**

4-(1,1-diphenylethyl)phenol (**2b**)

Into a 200 ml of three-necked flask, anisole (1.1g, 10mmol), 1,1-diphenylethanol (2.0 g, 10mmol) and polyphosphoric acid (20 g, 200mmol) were poured. It was heated with stirring at 100 °C for 23 hours. After cooling to rt, the reaction mixture was extracted with diethylether and washed with NaCl saturated aqueous solution. The organic layer was dried over sodium sulfate and the evaporated in vacuo. Into a 100 ml of three-necked flask, 2.5g 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 0.68g of ochreous solid was obtained in a 25% yield.

IR(KBr): 3487 (Ar-OH) cm^{-1}

¹H-NMR (DMSO-*d*₆: TMS) δ 2.32(3H, s, -CH₃), 7.02~7.24(14H, m, aromatic -H), 9.44(1H, s, O-H)

4-(4-tritylphenoxy)benzoic acid (**3a**)

A 100 ml of three-necked flask with a condenser was dried by a heat gun under nitrogen atmosphere. Into this flask, *p*-nitrobenzoic acid (0.18 g, 1.1mmol), freshly distilled dry DMF (5 ml), K₂CO₃ (0.35 g, 2.5mmol), and 4-triphenylmethylphenol (**2a**: 0.44 g, 1.3mmol) was poured. It was heated with stirring under 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 sulphate and dried in vacuo. The residue was recrystallised from ethanol to afford 0.33 g of white solid in a 67% yield. M.p.: see Table 2.

IR(KBr): 3489 (-OH), 1710 (C=O), 1280 (ether) cm⁻¹

¹H-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-PhOBA)₃Tb·2MeOH (**4a**)

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

(2Ph-PhOBA)₃Tb·2MeOH (**4b**)

As the same manner as **4a**, it could be prepared to afford 0.30g of white crystal in a 65% yield.

(1Ph-PhOBA)₃Tb·2MeOH (**4c**)

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

(0Ph-PhOBA)₃Tb·4MeOH (**4d**)

As the same manner as **4c**, it could be prepared to afford 0.20g of white crystal in a 55% yield.

Table 1 Elemental analysis data of (nPh-PhOBA)₃Tb·mMeOH, **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)

2-2. Measurements

The compounds synthesized here were identified by using FT-IR (Nicolet NEXUS670 FT-IR), ¹H-NMR (BRUKER DRX-400), elemental analysis (Perkin-Elmer elemental analyzer 2400), and thermogravimetry analysis (Rigaku Thermo plus TG8120). Phase transition behaviour of the present compounds (**3a~d** and **4a~d**) was observed with 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 adopted a Mettler FP82HT hot stage. Figs. 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 monochromators to produce point X-ray beam (diameter = 1.0 mm). The point beam runs through holes of the temperature-variable sample holder. As illustrated in Fig. S2, into the temperature-variable sample holder of 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 by using a Horiba Fluorolog FL3-21-NIR-OS spectrofluorometer equipped with a handmade hot plate¹⁵ 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,d** by using a single reaction solvent of MeOH. On the other hand, it was not successful for **4a,b** by using the single solvent of MeOH. It was attributable to the low solubilities of **3a,b** in pure MeOH which were resulted from the big 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,b**, the metallation successfully took place to afford the terbium complexes **4a,b**.

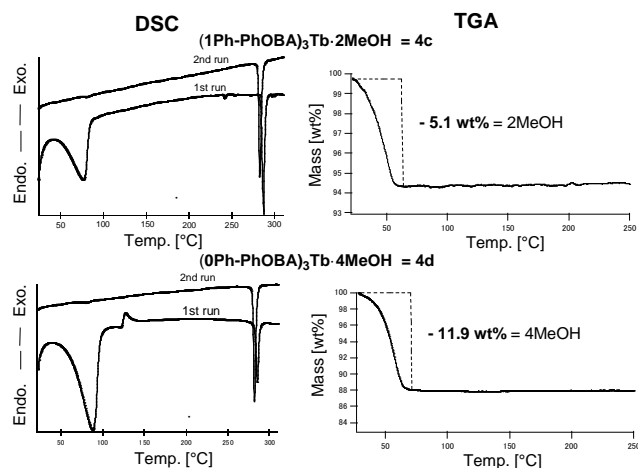


Fig. 3 DSC and TGA thermograms of (1Ph-PhOBA)₃Tb·2MeOH (**4c**) and (0Ph-PhOBA)₃Tb·4MeOH (**4d**)

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 thermogravimetry analyses (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,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).

3-2. Mesomorphic properties

The phase transition sequences for the flying-seed-like calamitic phenoxybenzoic acid derivatives **nPh-PhOBA** (**3a~d**) and their corresponding desolvated Mitsubishi-Mark-shaped terbium complexes (**nPh-PhOBA**)₃Tb (**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 mesomorphism¹⁶⁻¹⁸. The present phenoxybenzoic acid derivatives **nPh-PhOBA** (**3a~d**) may also form dimers as illustrated in Scheme 1.

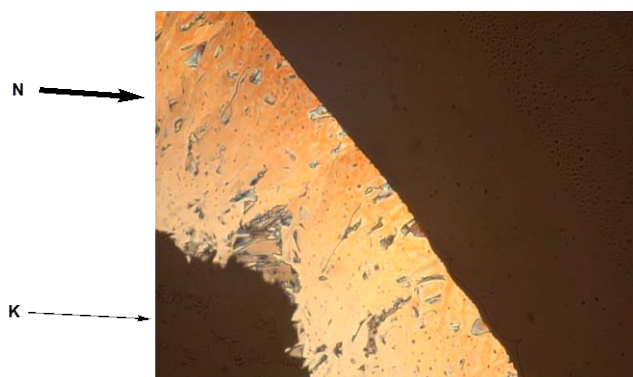


Fig. 4 Photomicrograph of **0Ph-PhOBA** (**3d**) at 220 °C. The crystalline phase K was changing into an unidentified mesophase (*M_x*) showing a marble texture.

As can be seen from this table, 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 heating from rt, it completely sublimated and disappeared before reaching the mesophase temperature range.

Therefore, the sample was inserted into the hot stage preheated at a certain temperature under the clearing point (= cp) of 246 °C. The set temperature was lowered little by little from the cp and observed by the POM step by step. At last we could observe the liquid-crystalline texture at 220 °C as shown a photomicrograph in Fig. 4. As can be seen from this photomicrograph, the crystalline phase K was changing into a marble texture with fluidity characteristic to a nematic phase¹⁹. However, it rapidly sublimated within one minute so that the mesophase could not be identified unambiguously. Hence, 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 between 220* and 246 °C of **3d** seems to be too big 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

Table 2 Phase transition sequences for the flying-seed-like calamitic **nPh-PhOBA** (**3a~d**), and desolvated Mitsubishi-Mark-shaped (**nPh-PhOBA**)₃Tb (**4a~d**) liquid crystals

Compound	Phase [#]	$T(^{\circ}\text{C})$ [$\Delta H(\text{kJ/mol})$]	Phase
3a	K	288[73.0]	I.L.(Subl.)
3b	K	176[94.7]	I.L.(Subl.)
3c	K	193[94.8]	I.L.(Subl.)
3d	K	220* → [167] → 246	<i>M_x</i> → I.L.(Subl.)
4a	K	356	dc
4b	K	334	dc
4c	K	286 [44.1] → Col _r (P2 ₁ /a) → 314	dc
4d	K	282 [35.5] → Col _r (P2 _m) → 308	dc

[#] Phase nomenclature: K = crystal, *M_x* = unidentified mesophase, Col_r = rectangular columnar mesophase, I.L.(Subl.) = isotropic liquid (accompanied by vigorous sublimation) and dc = decomposition.

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.

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 core in comparison with the

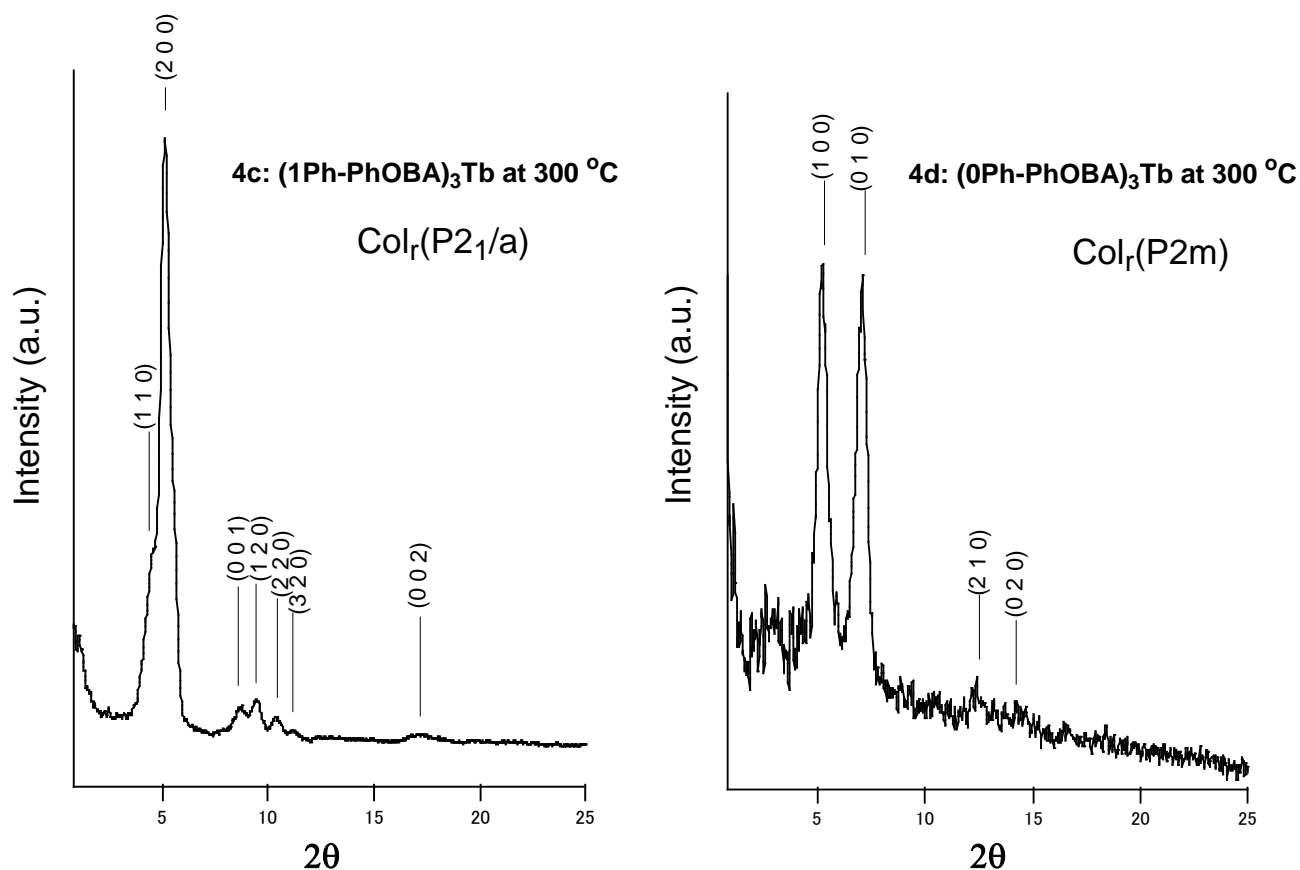


Fig. 5 X-ray diffraction patterns of (1Ph-PhOBA)₃Tb (**4c**) and (0Ph-PhOBA)₃Tb (**4d**) at 300°C.

Table 3 X-ray data of (1Ph-PhOBA)₃Tb (**4c**) and (0Ph-PhOBA)₃Tb (**4d**).

Compound Mesophase	Spacing/Å		Miller indices (<i>h k l</i>)
	Observed	Calculated	
4c: (1Ph-PhOBA)₃Tb			
Col _r (P2 ₁ /a) at 300°C	19.6	19.6	(2 0 0)
a = 39.2Å	17.3	17.3	(1 1 0)
b = 19.3Å	10.1	10.1	(0 0 1) ^{##}
c = 10.1Å	9.37	9.36	(1 2 0)
Z = 4.0 for ρ = 1.00*	8.53	8.64	(2 2 0)
	7.87	7.75	(3 2 0)
	5.14	5.07	(0 0 2) [#]
4d: (0Ph-PhOBA)₃Tb			
Col _r (P2m) at 300°C	16.9	16.9	(1 0 0)
a = 16.9Å	12.5	12.5	(0 1 0)
b = 12.5Å	7.14	6.99	(2 1 0)
	6.20	6.23	(0 2 0)

^{##} =stacking distance between dimers. [#] =stacking distance between monomers. * = assumed value.

bulkier substituents. Thus, these flying-seed-like compounds

suggest that the balance of core size and bulkiness of substituents is very important to obtain mesomorphism.

Mesomorphism of (nPh-PhOBA)₃Tb(III) (n=1, 0: **4c,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 acids derivatives nPh-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)₃Tb(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)₄PcCu (n=0~3) in our previous work was induced by all the bulky substituents **a**, **b**, **c** and **d** (n=0~3)¹². Therefore, balance of core size and bulkiness of substituents is very important to obtain mesomorphism for flying-seed-like compounds.

Fig. 5 shows the X-ray diffraction patterns of **4c** and **4d** at 300 °C. These 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, Col_r(P2₁/a) and Col_r(P2m), respectively. The small symmetrical difference between them may be originated from the difference of

bulkiness of the substituted groups of **c** and **d**. Interestingly, (1Ph-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 crystals¹².

3-3. Temperature-dependent fluorescence spectra

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

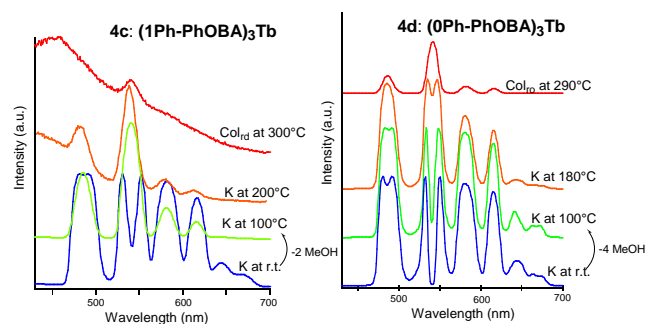


Fig.6 Temperature-dependent fluorescence spectra of (1Ph-PhOBA)₃Tb·2MeOH (**4c**) and (0Ph-PhOBA)₃Tb·4MeOH (**4d**).

increasing temperature^{20–22}. Big deformation of the spectrum of **4c** at 300 °C corresponds to considerable decomposition of the sample in the air for the long measurement time. The decomposition temperature 314 °C listed in Table 2 was the measured value with TGA under nitrogen atmosphere. The present temperature-dependent fluorescence spectral measurements were carried out in the air for long time. Therefore, the decomposition in the air started even at temperatures lower than the TGA decomposition temperatures, and progressed for long time. As the matter of fact, the colour of the sample measured at 300 °C changed from white to brown.

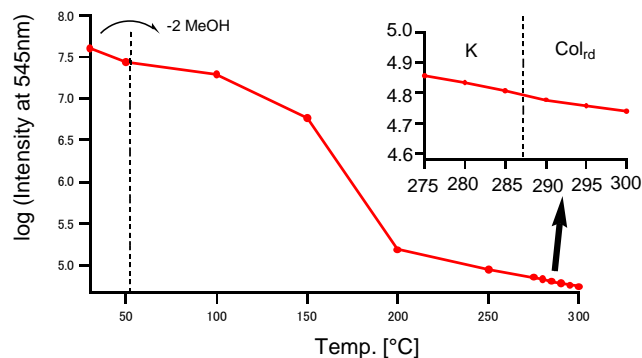
Although there have been several reports that the fluorescence intensities change with phase transitions^{20–23}, the present terbium complexes did not show discernible drastic changes for their desolventizing and phase transitions, as can be seen from Figure 7. Therefore, the fluorescence spectral changes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

4. Conclusion

We have synthesized novel flying-seed-like calamitic phenoxybenzoic acid derivatives, **nPh-PhOBA** (**3a–d**), and their Mitsubishi-Mark-shaped terbium complexes, (**nPh-PhOBA**)₃Tb·**mMeOH** (**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 flying-seed-like calamitic liquid crystal,

4c: (1Ph-PhOBA)₃Tb·2MeOH



4d: (0Ph-PhOBA)₃Tb·4MeOH

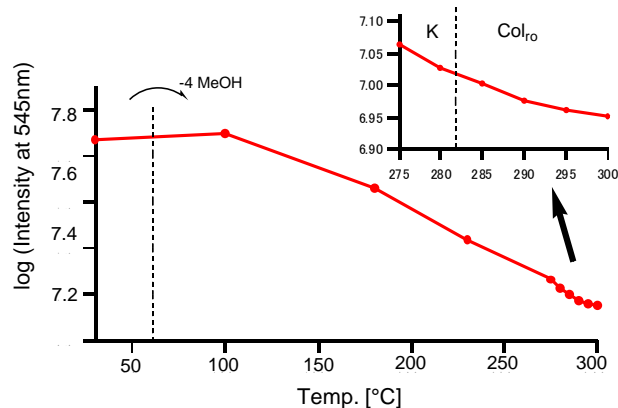


Fig.7 Fluorescent intensities at 545nm versus temperature for (1Ph-PhOBA)₃Tb·2MeOH (**4c**) and (0Ph-PhOBA)₃Tb·4MeOH (**4d**).

so 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 rectangular columnar mesophases Col_r(P2₁/a) and Col_r(P2m), respectively. It is very interesting that the PcCu complexes (**nPh-PhOBA**)₄PcCu 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 substitution of bulky groups instead of long alkyl chains, and that balance of core size and bulkiness of 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.

Notes

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[†] Part 2: Ref. 12 in this paper.

References

1. D. Vorländer, *Ber. Dtsch. Chem. Ges.*, 1911, **43**, 3120-3125

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2. D. Demus, H. Sackmann and K. Seibert, *Wiss. Z. Univ. Halle, Math.-Nat. R.* 1970, **19**, 47-62.
 3. P. Ferloni, M. Sanesi, P. L. Tonelli and P. Franzosini, *Z. Naturforsch.*, 1978, **33**, 240-242.
 - 5 4. M. Sanesi, P. Ferloni, G. Spinolo and P. L. Tonelli, *Z. Naturforsch.*, 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.
 - 10 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.
 - 15 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.
 - 20 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. Mitsubishi-Mark: see <http://www.mitsubishi.com/e/group/mark.html>.
 - 25 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.*, 1998, **317**, 153-164.
 - 30 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.
 - 35 19. D. M. Small, M. C. Bourges and D. G. Dervichian, *Biochim. Biophys. Acta*, 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.
 - 40 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.
 - 45 23. R. Cristian, J. Eccher, I. H. Bechtold, C. N. Tironi, A. A. Vieira, F. Molin and H. Gallardo, *Langmuir*, 2012, **28**, 11590-11598.