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Synthesis and Properties of Liquid Crystalline Organogelators with Cholesteryl 4-(4′-Alkoxybenzoylamino)benzoates

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As a new liquid-crystalline organogelator, cholesteryl 4-(4′-alkoxybenzoylamino)benzoates were prepared. Cholesteryl 4-(4′-alkoxybenzoylamino)benzoates had enantiotropic cholesteric and chiral smectic C phases. Furthermore, cholesteryl 4-(4′-alkoxybenzoylamino)benzoate gelled organic liquid such as *n*-decane, *n*-hexadecene, 1-butanol, 1-hexanol, 1-decanol, toluene, salad oil, linalool, geraniol, nerol, citronellol, limonene, linalyl acetate, lavender oil, orange oil, and lemon oil. The terpene gels show good release of the volatile components for a long period.

Self-assembled systems are of great importance, particularly for their potential application to nanomaterials such as liquid crystals and gelators.[1–4] Many studies have been reported on their structure and mechanisms of molecular aggregation. More than 110000 liquid-crystalline compounds have been reported to date.[5] To design a liquid-crystalline molecule, a rigid core and flexible alkyl side chains are required.[6] The number of organogelators has rapidly increased over the last 20 years.[1–3] In the past, new organogelators were often discovered accidentally, and studies were dedicated to understanding the relationship between the structure of a gelator and its gelation behavior. The aggregation of organogelators into fibrous networks is driven by multiple weak interactions such as dipole–dipole, van der Waals, hydrogen-bonding, and π-stacking interactions. Gelators are commonly classified by their driving force for molecular aggregation: non-hydrogen-bond-based and hydrogen-bond-based gelators. Amide compounds such as amino acid and urea and hydroxy compounds such as 12-hydroxystearic acid and sugars are hydrogen-bond-based gelators, whereas anthracene, cholesterol, and tropone derivatives are non-hydrogen-bond-based gelators. Recently, we have reported several liquid-crystalline organogelators called "organogelling liquid crystal."[7–10] Several organogelling liquid crystals, octaalkoxy-substituted α-diketonatocopper complex,[11] octa(dodecyl)tetrapyrazinoporphyrazine,[12] 3,4,5-trialkoxybenzoylamine derivatives,[9,13–24] 3,4,5-trialkoxybenzyl derivatives,[25,26] 2,3,6,7,10,11-hexaalkoxytriphenylene derivatives,[10,27–29] dibenzophenazine derivatives,[30,31] hydrazine derivatives,[32–34] 4-cyanophenyl 4-*n*-alkoxybenzoates,[10] 4-cyano-4′-alkoxybiphenyls,[10] 4,4′-dialkanoyloxybiphenyls,[10] azoxybenzene derivatives,[10] coumarin derivatives,[35,36] cholesteryl alkanoate derivatives,[10,37–39] and cholesteryl 4-alkoxybenzoates **1** (Figure 1)[10] have been reported. Compound **1** exhibits enantiotropic cholesteric and smectic A phases and gels organic solvents such as 1-decanol and *n*-hexadecane. However, **1** could not be used for gel preparation at low concentration. In this paper, we report the mesomorphic and gelation properties of cholesteryl 4-(4′-alkoxybenzoylamino)-benzoates **2** as new liquid-crystalline organogelators with cholesteryl benzoate and hydrogen-bonding groups and its application to terpene and perfume gels.

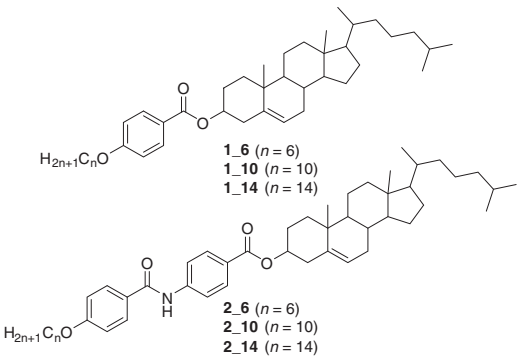

Figure 1. Chemical structures of **1** and **2**.

Cholesteryl 4-(alkanoylamino)benzoates **2** were prepared by the esterification of cholesterol with the corresponding 4-(4′-alkoxybenzoylamino)benzoic acid in the presence of EDC·HCl (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride) and DMAP (4-(dimethylamino)pyridine). The structures and purities of the compounds **2** were ascertained by NMR spectroscopy and elemental analysis.[40]

The transition temperatures and thermal behaviors of **2** were determined using a differential scanning calorimeter, a polarizing microscope equipped with a hot stage, and an X-ray diffractometer. The optical micrographs of chiral smectic C (SmC*) phase and cholesteric (N*) phase of **2_14** are shown in Figure 2.

Chiral smectic C and cholesteric phases were determined from a following observation and an X-ray diffraction study, i.e., broken focal-conic fan, banded focal-conic fan, and schlieren textures for chiral smectic C phase;[41] Grandjean steps at the border and oily streak textures for the cholesteric phase. The thermal behaviors of the cholesteryl benzoates **1** and **2** are summarized in Table 1. Compounds **2** had a phase sequence of Cr–SmC*–N*–Isotropic (Iso), whereas **1** had a phase sequence of Cr–SmA–N*–Iso.[7] The melting and clearing points of **2** were higher than those of the corresponding derivatives **1**. This means that the hydrogen bonds of benzoylamide group strengthen the intermolecular interactions.

We measured the X-ray diffraction pattern of the mesophases. The smectic layer spacings (*d*) and molecular lengths (*l*) of **2** are listed in Table 2. The molecular lengths (*l*) of **2** were calculated by the MM2 method. The *d*/*l* ratios of chiral smectic C (SmC*) phase of **2** are 0.73 for **2_10** and 0.69 for **2_14**. This

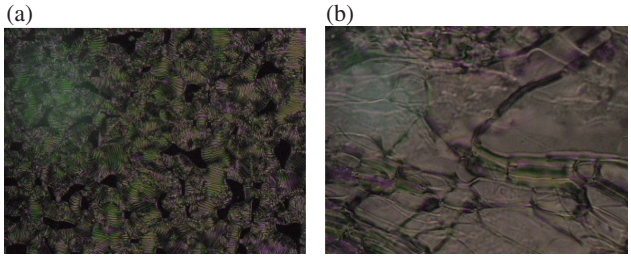

Figure 2. Optical cross-polarizing micrographs of **2_14** at (a) 225 (SmC*) and (b) 245 °C (N*). All pictures taken on cooling from the isotropic phase.

Table 1. Transition temperatures (°C) of **1** and **2**

Compounds	*n*	Transition temperatures/°C
1_6	6	Cr_1 • 113.5 • Cr_2 • 150.9 • N* • 229.9 • Iso
1_10	10	Cr • 110.4 • SmA • 177.7 • N* • 208.1 • Iso
1_14	14	Cr • 117.6 • SmA • 175.9 • N* • 190.2 • Iso
2_6	6	Cr • 231.4 • N* • 301.7 • Dec
2_10	10	Cr • 216.1 • SmC* • 254.1 • N* • 264.4 • Iso
2_14	14	Cr • 201.4 • SmC* • 239.4 • N* • 246.6 • Iso

Table 2. Layer spacings (Å) and molecular lengths (Å) of **2**

Compounds	Temperatures /°C	Layer spacings (*d*) /Å	Molecular lengths (*l*) /Å
2_10	220	30.5	41.7
2_14	230	32.3	46.5

result suggests that the molecular long axes of **2** are tilted at 47° for **2_10** and 44° for **2_14**, with respect to the normal to the layer in the SmC* phase and form the layer.

We carried out the gelation test of **2** in various organic solvents (*n*-hexane, *n*-decane, *n*-hexadecane, cyclohexane, methanol, ethanol, 1-butanol, 1-hexanol, 1-decanol, ethyl acetate, acetonitrile, THF, benzene, toluene, and salad oil). The result of the gelation test with **2** is shown in Table 3. Compounds **2** gelled *n*-decane, *n*-hexadecene, 1-butanol, 1-hexanol, 1-decanol, toluene, and salad oil, while **1** gelled 1-decanol and *n*-hexadecane.

Figure 3 shows a photograph of **2_10**–decanol gel and an optical micrograph of the gel phase of **2_10** in 1-decanol (0.9 w/v%) recorded at 25 °C on cooling from an isotropic liquid state. Highly intertwined, rod-like fibers aligned to form the network structures by making bundles with diameters of ca. 1–4 μm. The minimum gel concentrations (MGC, g dm^{-3}) of **2** are 40 for **2_6**–*n*-hexadecene, 4 for **2_10**–*n*-hexadecene, 49 for **2_14**–*n*-hexadecene, 4 for **2_6**–1-decanol, 3 for **2_10**–1-decanol, and 4 for **2_14**–1-decanol. The gelation ability of **2_10** for 1-decanol and *n*-hexadecane is superior than that of the other cholesteryl benzoates.

In order to evaluate the hydrogen bonding in the gels, the IR spectra of crystalline, 1-decanol gel (5.0 w/v%), and a chloroform solution of **2_10** were measured. The absorption band at 1655 cm^{-1} of **2_10**–decanol gel was lower than that (1672 cm^{-1}) of the chloroform solution and close to that (1655 cm^{-1}) of crystalline compound. This means that the intermolecular

Table 3. Gelation ability of **2**[a]

	2_6	**2_10**	**2_14**
n-Hexane	Insol	Insol	Insol
n-Decane	Gel	Gel	Gel
n-Hexadecane	Gel	Gel	Gel
Cyclohexane	Insol	Insol	Insol
Methanol	Insol	Insol	Insol
Ethanol	Insol	Insol	Insol
1-Butanol	Gel	Gel	Gel
1-Hexanol	Gel	Gel	Gel
1-Decanol	Gel	Gel	Gel
Ethyl acetate	Insol	Insol	Insol
Acetonitrile	Cryst	Cryst	Cryst
THF	Cryst	Cryst	Gel
Benzene	Cryst	Cryst	Cryst
Toluene	Cryst	Gel	Gel
Salad oil	Gel	Gel	Gel

[a]Gel: gelation, Cryst: crystallization, and Insol: insoluble.

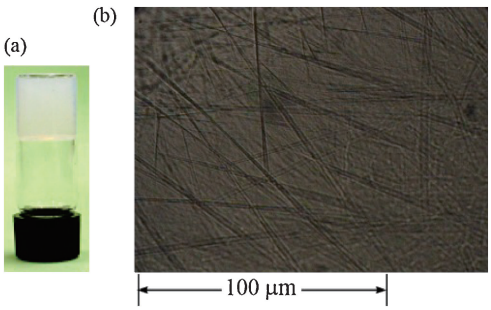

Figure 3. (a) Photograph and (b) micrograph of **2_10**–1-decanol gel.

hydrogen bonds of the amide group play an important role in the crystal and gel states.

To study the application of organogelator **2** to new materials, terpene and perfume gels were prepared. In perfume, fragrance, and deodorant materials, hydrogelators such as carrageenan, agar, collagen, gellan gum, gelatin, etc. have been used for gelations of water-containing terpenes, essential oils, and perfumes. Therefore, the purity of the oils in the gels is low and most of the components of these materials comprise water. Fortunately, under the gel–organic liquid conditions (5.5–6.8 mg/1.0 cm^3), **2_10** could gel the terpenoids such as linalool, geraniol, nerol, citronellol, limonene, linalyl acetate, and essential oils such as lavender oil, lemon oil, and orange oil as shown in Figure 4.

The release tests of the volatile components from **2_10**–limonene, –linalool, and –linallyl acetate gels were carried out. The caps of the glass tubes containing the fragrance gel were opened. They were left to stand at room temperature, and the weight changes of the gels and neat liquids were investigated, as shown in Table 4. The weights of the gels and neat liquids decreased with time. The rates of decrease in the weight of the gels were slower than those of neat liquids, showing that the gel state controlled the release of the volatile components. After 100 days, each gel maintained the gel state with a characteristic scent of terpenoids.

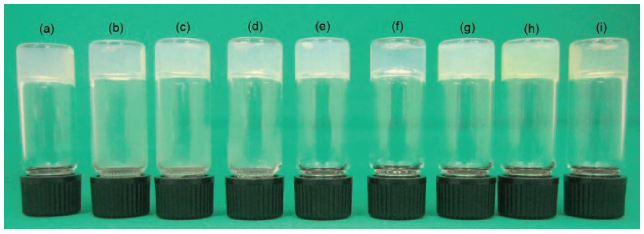

Figure 4. Photograph of (a) **2_10**–linalool, (b) **2_10**–geraniol, (c) **2_10**–nerol, (d) **2_10**–citronellol, (e) **2_10**–limonene, (f) **2_10**–linalyl acetate, (g) **2_10**–lavender oil, (h) **2_10**–lemon oil, and (i) **2_10**–orange oil gels.

Table 4. Weight changes (mg) of the terpene gels containing **2_10** and neat liquids by release tests of the volatile components

Solvents/Status	**2_10** /mg	Weight/mg		
		After 0 day	After 50 d	After 100 d
Limonene/Gel	6.4	825.2	446.7	323.4
Limonene/Liquid	0	827.6	434.8	283.1
Linallol/Gel	6.1	855.3	825.5	807.0
Linallol/Liquid	0	855.6	817.1	787.2
Linallyl acetate/Gel	6.8	872.0	852.0	841.0
Linallyl acetate/Liquid	0	872.2	848.9	830.2

Cholesteryl 4-(4′-decyloxybenzoylamino)benzoates (**2_10**) had mesomorphic and organogelation properties with good gelation ability for terpenes and essential oils. We succeeded in preparing perfume gels containing 99% or more of terpene and essential oil. The terpene gels showed good release of the volatile components for a long period. The gels may be utilized as fragrance and deodorant agents.

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40 **1_6**: ^{1}H NMR (270.05 MHz, $CDCl_3$): δ 0.69 (3H, s), 0.87 (6H, d, $J = 6.6$ Hz), 0.92 (3H, d, $J = 6.6$ Hz), 1.07 (3H, s), 0.85–2.03 (37H, m), 2.47 (2H, d, $J = 7.9$ Hz), 4.03 (2H, t, $J = 6.6$ Hz), 4.84 (1H, m), 5.42 (1H, d, $J = 3.9$ Hz), 7.05 (2H, d, $J = 8.9$ Hz), 7.72 (2H, d, $J = 8.6$ Hz), 7.84 (2H, d, $J = 8.9$ Hz), 7.85 (1H, s), 8.05 (2H, d, $J = 8.6$ Hz). Found: C, 79.42; H, 9.48; N, 1.95%. Calcd for $C_{47}H_{67}NO_4$: C, 79.50; H, 9.51; N, 1.97%. **1_10**: ^{1}H NMR (270.05 MHz, $CDCl_3$): δ 0.69 (3H, s), 0.86 (3H, d, $J = 6.6$ Hz), 0.87 (3H, d, $J = 6.6$ Hz), 0.92 (3H, d, $J = 6.6$ Hz), 1.07 (3H, s), 0.85–2.05 (45H, m), 2.47 (2H, d, $J = 7.6$ Hz), 4.02 (2H, t, $J = 6.6$ Hz), 4.84 (1H, m), 5.42 (1H, d, $J = 3.9$ Hz), 6.97 (2H, d, $J = 8.9$ Hz), 7.72 (2H, d, $J = 8.9$ Hz), 7.84 (2H, d, $J = 8.9$ Hz), 7.86 (1H, s), 8.05 (2H, d, $J = 8.9$ Hz). Found: C, 79.64; H, 9.86; N, 1.79% Calcd for $C_{51}H_{75}NO_4$: C, 79.95; H, 9.87; N, 1.83. **1_14**: ^{1}H NMR (270.05 MHz, $CDCl_3$): δ 0.69 (3H, s), 0.87 (6H, d, $J = 6.9$ Hz), 0.92 (3H, d, $J = 6.6$ Hz), 1.07 (3H, s), 0.85–2.03 (53H, m), 2.47 (2H, d, $J = 7.9$ Hz), 4.02 (2H, t, $J = 6.6$ Hz), 4.85 (1H, m), 5.42 (1H, d, $J = 3.9$ Hz), 6.97 (2H, d, $J = 8.6$ Hz), 7.72 (2H, d, $J = 8.9$ Hz), 7.84 (2H, d, $J = 8.6$ Hz), 7.85 (1H, s), 8.06 (2H, d, $J = 8.6$ Hz). Found: C, 80.40; H, 10.18; N, 1.67%. Calcd for $C_{55}H_{83}NO_4$: C, 80.34; H, 10.17; N, 1.70%.
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