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| タイトル | 1つまたは2つのアルコキシトロポン基を有するモノアザクラウンおよびジアザクラウンエーテルの合成と性質 |
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# Synthesis and Characterization of Monoazacrown and Diazacrown Ethers Functionalized with One or Two Alkoxytropone Units

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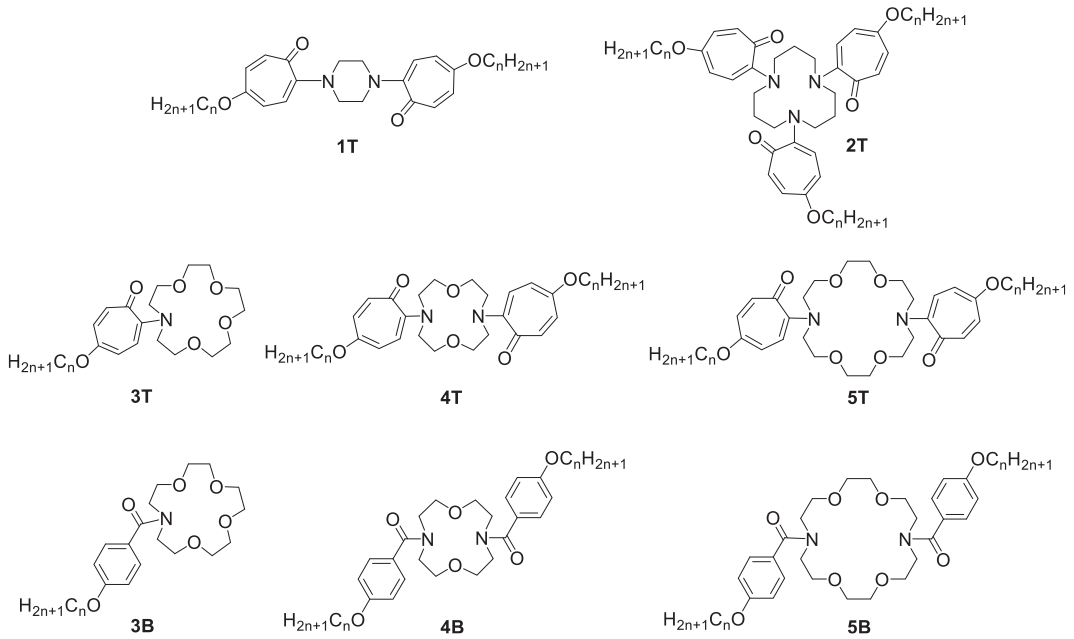
**Abstract**—Troponoid azacrown ether derivatives bearing long alkyl chains were synthesized through high-pressure reactions between 5-alkoxy-2-methoxytropone and various azacrown ethers, including 1-aza-15-crown-5, 4,10-diaza-12-crown-4, and 4,13-diaza-18-crown-6. The *N,N'*-di(tropon-2-yl)-diaza-18-crown-6 ether derivative (**5T12**) was found to form stable complexes with sodium dodecyl sulfate and silver dodecyl sulfate. While neither the troponoid nor the corresponding benzenoid derivatives exhibited intrinsic liquid crystalline behavior, the complexation of **5T12** with sodium dodecyl sulfate induced a monotropic mesophase.

## 1. Introduction

Since Pedersen's groundbreaking discovery of crown ethers in 1967, crown compounds have garnered significant attention due to their unprecedented structural and functional properties.[1] Extensive research has explored their complexation behavior, structural diversity, and physicochemical characteristics, culminating in the synthesis of numerous novel crown derivatives. These compounds have demonstrated remarkable versatility across a wide range of applications, including organic and polymer synthesis, metal ion capture and separation, ion-selective electrodes, analytical chemistry, chiral resolution using crown ethers, enzyme modeling, biochemistry, and the development of pharmaceutical and agrochemical agents.[2–4] Among these, discotic compounds incorporating azamacrocycles such as hexacyclen and cyclam as core structures have been investigated.[5,6] It has been reported that these azamacrocycle derivatives exhibit columnar (Col) phases depending on the ring size and the number and type of side chains. Subsequently, rod-like compounds containing crown ethers at the central or terminal positions of liquid crystalline molecules have also been reported.[7,8] Furthermore, exploiting the complexation ability of crown ethers, non-liquid crystalline azamacrocycle derivatives have been synthesized. Upon complexation with $Pd^{2+}$ or $K^{+}$ ions, these compounds exhibit liquid crystalline behavior, demonstrating the potential of metal-complex liquid crystals.[9,10] While troponoids—non-

benzenoid aromatic compounds featuring a seven-membered ring—have emerged as a unique class of molecules with distinctive electronic and conformational attributes.[11] Key representatives such as tropone, and tropolone exhibit notable reactivity and structural features that set them apart from conventional aromatic systems. Building on these properties, we have synthesized a variety of functional molecules incorporating troponoid frameworks, including crown ethers,[11–13] chromoionophores,[11,14–16] dyes,[11,17] liquid crystals,[11,18–24] and gelators. These designs leverage the inherent aromaticity and conformational flexibility of troponoids to achieve functionalities unattainable with traditional benzenoid compounds. Recently, we prepared liquid crystals with a *N,N'*-di(tropon-2-yl)piperazine core (**1T**)[19,21,22] and *N,N',N''*-tris(tropon-2-yl)-1,5,9-triazacyclododecane core (**2T**).[20] The piperazine derivatives (**1T**) had a smectic A (SmA) phase while the 1,5,9-triazacyclododecane derivatives (**2T**) had a bicontinuous cubic (Cub) phase with a *Pn3m* space group. In this paper, we report the synthesis of troponoid and benzenoid azacrown ether derivatives (**3T**-**5T**, **3B**-**5B**, scheme 1) bearing long alkyl chains—namely, aza-15-crown-5 ether, diaza-12-crown-4 ether, and diaza-18-crown-6 ether—and evaluate their mesomorphic properties.




Scheme 1

## 2. Experimental

### 2.1. Analysis

Elemental analyses were performed at the elemental analysis laboratory of Kyushu University. The NMR spectra were recorded using JEOL GSX 270H and Lambda 400 spectrometers and solutions in $CDCl_3$ at room temperature; the chemical shifts are expressed in $\delta$ units. The mass spectra were measured with JEOL 01SG-2 and JMS-700 spectrometers. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of ethyl acetate, chloroform, and hexane. The transition temperatures were measured by differential scanning calorimetry (Seiko DSC200) and the mesomorphic phases were observed by polarizing optical microscopy (Olympus BHSP BH-2 equipped with a Linkam TH-600MS hot stage). X-ray diffraction measurements were carried out with a Rigaku Rint 2100 system using Ni-filtered Cu-K$\alpha$ radiation at various temperatures. The measuring temperatures were controlled with a Linkam HFS-91 hot stage.

### 2.2. Material

#### 2.2.1. Synthesis of *N*-(5-alkoxytropone-2-yl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (3T)

A toluene solution (4 $cm^3$) of 1,4,7,10-tetraoxa-13-azacyclopentadecane (44.7 mg, 0.20 mmol) and 5-octyloxy-2-methoxytropone (169 mg, 0.64 mol) was heated at 100°C under 0.5 GPa. After 4 d, the solvent was removed under reduced pressure and the residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **3T_8** (66.5 mg, 74%) yellow oils.
**3T8** (74%), yellow oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (3H, *t*, *J*=6.8 Hz), 1.29-1.44 (10H, *m*), 1.76 (2H, *quint*, *J*=6.8 Hz), 3.63-3.67 (16H, *m*), 3.68-3.76 (4H, *m*), 3.87 (2H, *t*, *J*=6.8 Hz), 6.47 (1H, *d*, *J*=11.4 Hz), 6.86 (1H, *d*, *J*=11.4 Hz), 6.96 (2H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.6, 26.0, 29.1, 29.2, 29.3, 31.8, 52.9, 68.7 (2C), 69.7 (2C), 70.32 (2C), 70.33 (2C), 70.9 (2C), 112.3, 118.8, 130.0, 134.9, 152.4, 157.0, 181.0. FAB-MS: *m*/*z*, 452 ($M+H^+$). E. A. Found: C, 66.28; H, 9.13; N, 3.08%. Calcd for $C_{25}H_{41}NO_6$: C, 66.49; H, 9.13; N, 3.10%.
**3T12** (53%), yellow crystals, m.p. 121-122°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (3H, *t*, *J*=6.8 Hz), 1.27-1.43 (18H, *m*), 1.75 (2H, *quint*, *J*=6.8 Hz), 3.62-3.68 (16H, *m*), 3.73-3.76 (4H, *m*), 3.86 (2H, *t*, *J*=6.8 Hz), 6.47 (1H, *d*, *J*=11.4 Hz), 6.86 (1H, *d*, *J*=11.4 Hz), 6.96 (2H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.7, 26.0, 29.1, 29.3, 29.56, 29.59 (2C), 29.63, 29.7, 31.9, 53.0, 68.7 (2C), 69.8 (2C), 70.35 (2C), 70.37 (2C), 71.0 (2C), 112.3, 118.9, 130.1, 134.9, 152.5, 157.1, 181.1. FAB-MS: *m*/*z*, 508 ($M+H^+$). E. A. Found: C, 68.40; H, 9.66; N, 2.83%. Calcd for $C_{29}H_{49}NO_6$: C, 68.61; H, 9.73; N, 2.76%.
**3T16** (73%) yellow crystals, m.p. 69-70°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (3H, *t*, *J*=6.8 Hz), 1.21-

1.43 (26H, *m*), 1.75 (2H, *quint*, *J*=6.8 Hz), 3.62-3.68 (16H, *m*), 3.73-3.76 (4H, *m*), 3.86 (2H, *t*, *J*=6.8 Hz), 6.47 (1H, *d*, *J*=11.4 Hz), 6.86 (1H, *d*, *J*=11.4 Hz), 6.96 (2H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.7, 26.0, 29.1, 29.4 (2C), 29.57 (2C), 29.60 (2C), 29.67 (2C), 29.7 (2C), 31.9, 53.0, 68.7 (2C), 69.8 (2C), 70.36 (2C), 70.38 (2C), 71.0 (2C), 112.3, 118.8, 130.0, 134.9, 152.5, 157.10, 181.1. FAB-MS: *m/z*, 564 ($M+H^+$). E. A. Found: C, 70.17; H, 10.16; N, 2.45%. Calcd for $C_{33}H_{57}NO_6$: C, 70.30; H, 10.19; N, 2.48%.

### 2.2.2. Synthesis of *N,N'*-bis(5-alkoxytropone-2-yl)-1,7-dioxa-4,10-diazacyclododecane (4T)

A toluene solution (4 $cm^3$) of 1,7-dioxa-4,10-diazacyclododecane (25.1 mg, 0.14 mmol) and 5-octyloxy-2-methoxytropone (199 mg, 0.75 mol) was heated at 100°C under 0.5 GPa. After 4 d, the solvent was removed under reduced pressure and the residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **4T8** (46.6 mg, 51%) yellow crystals.

**4T8** (51%) yellow crystals, m.p. 100-101°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (6H, *t*, *J*=6.8 Hz), 1.29-1.43 (20H, *m*), 1.75 (4H, *quint*, *J*=6.8 Hz), 3.63 (16H, *s*), 3.85 (4H, *t*, *J*=6.8 Hz), 6.41 (2H, *d*, *J*=11.4 Hz), 6.97 (4H, *s*), 7.04 (2H, *d*, *J*=11.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.16 (2C), 29.23 (2C), 29.3 (2C), 31.8 (2C), 53.0 (4C), 68.6 (2C), 70.0 (4C), 112.2 (2C), 122.0 (2C), 130.1 (2C), 135.6 (2C), 152.5 (2C), 157.6 (2C), 181.5 (2C). FAB-MS: *m/z*, 639 ($M+H^+$). E. A. Found: C, 71.38; H, 9.32; N, 3.68%. Calcd for $C_{38}H_{58}N_2O_6$: C, 71.44; H, 9.15; N, 4.38%.

**4T12** (36%) yellow crystals, m.p. 105-106°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (6H, *t*, *J*=6.8 Hz), 1.27-1.43 (36H, *m*), 1.75 (4H, *quint*, *J*=6.8 Hz), 3.63 (16H, *brs*), 3.85 (4H, *t*, *J*=6.8 Hz), 6.40 (2H, *d*, *J*=11.4 Hz), 6.96 (4H, *dd*, *J*=14.6, 12.8 Hz), 7.04 (2H, *d*, *J*=11.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.1 (2C), 29.32 (2C), 29.34 (2C), 29.54 (2C), 29.57 (2C), 29.61 (2C), 29.63 (2C), 31.9 (2C), 53.0 (4C), 68.6 (2C), 70.0 (4C), 112.2 (2C), 122.0 (2C), 130.1 (2C), 135.6 (2C), 152.5 (2C), 157.6 (2C), 181.5 (2C). FAB-MS: *m/z*, 751 ($M+H^+$). E. A. Found: C, 73.43; H, 9.96; N, 3.73%, Calcd for $C_{46}H_{74}N_2O_6$: C, 73.56; H, 9.93; N, 3.73%.

**4T16** (34%) yellow crystals, m.p. 101-102°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.26-1.43 (52H, *m*), 1.74 (4H, *quint*, *J*=6.8 Hz), 3.63 (16H, *brs*), 3.84 (4H, *t*, *J*=6.8 Hz), 6.40 (2H, *d*, *J*=11.4 Hz), 6.97 (4H, *s*), 7.05 (2H, *d*, *J*=11.4 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.1 (2C), 29.4 (2C), 29.56 (4C), 29.59 (4C), 29.65 (4C), 29.68 (4C), 31.9 (2C), 53.0 (4C), 68.6 (2C), 70.0 (4C), 112.1 (2C), 122.0 (2C), 130.1 (2C), 135.6 (2C), 152.5 (2C), 157.6 (2C), 181.5 (2C). FAB-MS: *m/z*, 863 ($M+H^+$). E. A. Found: C, 74.87; H, 10.39; N, 3.31%, Calcd for $C_{54}H_{90}N_2O_6$: C, 75.13; H, 10.51; N, 3.24%.

### 2.2.3. Synthesis of *N,N'*-bis(5-alkoxytropone-2-yl)-1,4,10,13-tetraoxa-7,16-diazacyclooctadecene (5T)

A toluene solution (4 $cm^3$) of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecene (55.5 mg, 0.21 mmol)

and 5-octyloxy-2-methoxytropone (556.3 mg, 2.10 mol) was heated at 100°C under 0.5 GPa. After 4 d, the solvent was removed under reduced pressure, and the residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **5T8** (76.9 mg, 50%) yellow crystals.

**5T8** (50%) yellow crystals, m.p. 66-67°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (6H, *t*, *J*=6.8 Hz), 1.29-1.45 (20H, *m*), 1.76 (4H, *quin*t, *J*=6.8 Hz), 3.58 (8H, *s*), 3.69 (16H, *s*), 3.87 (4H, *t*, *J*=6.8 Hz), 6.45 (2H, *d*, *J*=11.2 Hz), 6.87 (2H, *d*, *J*=11.2 Hz), 6.97 (4H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.6 (2C), 25.8 (2C), 29.1 (2C), 29.2 (2C), 29.3 (2C), 31.8 (2C), 52.0 (4C), 68.6 (2C), 69.9 (4C), 70.6 (4C), 112.2 (2C), 122.1 (2C), 130.3 (2C), 135.5 (2C), 152.4 (2C), 157.5 (2C), 181.2 (2C). FAB-MS: *m*/*z*, 727 (M+H$^+$). E. A. Found: C, 69.12; H, 9.15; N, 3.71%, Calcd for $C_{42}H_{66}N_2O_8$: C, 69.39; H, 9.15; N, 3.85%.

**5T12** (41%) yellow crystals, m.p. 76-77°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.27-1.43 (36H, *m*), 1.76 (4H, *quint*, *J*=6.8 Hz), 3.58 (8H, *s*), 3.69 (16H, *s*), 3.86 (4H, *t*, *J*=6.8 Hz), 6.45 (2H, *d*, *J*=11.2 Hz), 6.87 (2H, *d*, *J*=11.2 Hz), 6.99 (4H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.1 (2C), 29.3 (2C), 29.56 (2C), 29.59 (4C), 29.63 (2C), 29.7 (2C), 31.9 (2C), 52.0 (2C), 68.7 (4C), 69.9 (4C), 70.6 (4C), 111.7 (2C), 120.1 (2C), 130.6 (2C), 135.5 (2C), 152.4 (2C), 157.6 (2C), 181.3 (2C). FAB-MS: *m*/*z*, 839 (M+H$^+$). E. A. Found: C, 71.50; H, 9.88; N, 3.30%, Calcd for $C_{50}H_{82}N_2O_8$: C, 71.56; H, 9.85; N, 3.34%.

**5T16** (65%) yellow crystals, m.p. 86-87°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.26-1.43 (52H, *m*), 1.76 (4H, *quint*, *J*=6.8 Hz), 3.58 (8H, *s*), 3.69 (16H, *s*), 3.86 (4H, *t*, *J*=6.8 Hz), 6.45 (2H, *d*, *J*=11.2 Hz), 6.87 (2H, *d*, *J*=11.2 Hz), 6.97 (4H, *brs*). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.1 (2C), 29.3 (4C), 29.5 (4C), 29.57 (4C), 29.64 (4C), 29.7 (4C), 31.9 (2C), 52.0 (2C), 68.6 (4C), 69.9 (4C), 70.6 (4C), 111.6 (2C), 120.1 (2C), 130.3 (2C), 135.5 (2C), 152.4 (2C), 157.5 (2C), 181.2 (2C). FAB-MS: *m*/*z*, 961 (M+H$^+$). E. A. Found: C, 73.07; H, 10.38; N, 2.91%, Calcd for $C_{58}H_{98}N_2O_8$: C, 73.22; H, 10.38; N, 2.94%.

### 2.2.4. Synthesis of *N*-(4-alkoxybenzoyl)-1,4,7,10-tetraoxa-13-azacyclopentadecane (3B)

A thionyl chloride solution (0.5 cm$^3$) of 4-octyloxybenzoic acid (55.8 mg, 0.22 mmol) was refluxed for 3 h. After excess thionyl chloride was removed, a pyridine solution (3 cm$^3$) of 1,4,7,10-tetraoxa-13-azacyclopentadecane (26.8 mg, 0.12 mmol) and a catalytic amount of DMAP was refluxed for 12 h, The reaction mixture was poured into $KHSO_4$ solution and extracted with ethyl acetate. After being dried on $MgSO_4$, the solvent was removed under reduced pressure. The residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **3B8** (41.4 mg, 76%) colorless oils.

**3B8** (76%), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (3H, *t*, *J*=6.8 Hz), 1.26-1.49 (10H, *m*), 1.78

(2H, *quint*, *J*=6.8 Hz), 3.54-3.76 (20H, *m*), 3.96 (2H, *t*, *J*=6.8 Hz), 6.88 (2H, *d*, *J*=8.7 Hz), 7.37 (2H, *d*, *J*=8.7 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.6, 26.0, 29.15, 29.19 (2C), 29.3, 31.8, 68.0 (2C), 70.26 (4C), 70.29 (4C), 114.2 (2C), 128.5 (2C), 128.7, 160.0, 172.2. FAB-MS: *m*/*z*, 452 ($M+H^+$). E. A. Found: C, 65.33; H, 9.11; N, 2.99%, Calcd for $C_{25}H_{41}NO_6 \cdot 0.5H_2O$: C, 65.19; H, 9.19; N, 3.04%.

**3B12** (74%), colorless oil. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (3H, *t*, *J*=6.8 Hz), 1.24-1.47 (18H, *m*), 1.78 (2H, *quint*, *J*=6.8 Hz), 3.53-3.76 (20H, *m*), 3.96 (2H, *t*, *J*=6.8 Hz), 6.87 (2H, *d*, *J*=8.7 Hz), 7.37 (2H, *d*, *J*=8.7 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.6, 26.0, 29.1, 29.28, 29.33, 29.51, 29.54, 29.57 (2C), 29.60, 31.9, 68.0 (2C), 70.2 (4C), 70.3 (4C), 114.1 (2C), 128.5 (2C), 128.7, 160.0, 172.2. FAB-MS: *m*/*z*, 508 ($M+H^+$). E. A. Found: C, 67.48; H, 9.66; N, 2.62%, Calcd for $C_{29}H_{49}NO_6 \cdot 0.5H_2O$: C, 67.41; H, 9.75; N, 2.71%.

**3B16** (51%), colorless crystals, m.p. 58-59°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (3H, *t*, *J*=6.8 Hz), 1.26-1.45 (26H, *m*), 1.78 (2H, *quint*, *J*=6.8 Hz), 3.54-3.76 (20H, *m*), 3.96 (2H, *t*, *J*=6.8 Hz), 6.87 (2H, *d*, *J*=8.7 Hz), 7.36 (2H, *d*, *J*=8.7 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1, 22.7, 26.0, 29.2, 29.33, 29.36, 29.55, 29.57 (2C), 29.63 (2C), 29.7 (4C), 31.9, 68.0 (2C), 70.3 (8C), 114.1 (2C), 128.5 (2C), 128.7, 160.0, 172.2. FAB-MS: *m*/*z*, 564 ($M+H^+$). E. A. Found: C, 69.29; H, 10.09; N, 2.44%, Calcd for $C_{33}H_{57}NO_6 \cdot 0.5H_2O$: C, 69.19; H, 10.21; N, 2.45%.

### 2.2.5. Synthesis of *N,N'*-Bis(4-alkoxybenzoyl)-1,7-dioxa-4,10-diazacyclododecane (4B)

A thionyl chloride solution (0.5 $cm^3$) of 4-octyloxybenzoic acid (102.1 mg, 0.41 mmol) was refluxed for 3 h. After excess thionyl chloride was removed, a pyridine solution (3 $cm^3$) of 1,7-dioxa-4,10-diazacyclododecane (19.6 mg, 0.11 mmol) and a catalytic amount of DMAP was refluxed for 12 h, The reaction mixture was poured into $KHSO_4$ solution and extracted with ethyl acetate. After being dried on $MgSO_4$, the solvent was removed under reduced pressure. The residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **4B8** (48.4 mg, 69%) colorless crystals.

**4B8** (69%), colorless crystals, m.p. 68-69°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.90 (6H, *t*, *J*=6.8 Hz), 1.26-1.48 (20H, *m*), 1.78 (4H, *quint*, *J*=6.8 Hz), 3.58-3.86 (16H, *m*), 3.96 (4H, *t*, *J*=6.8 Hz), 6.87 (4H, *d*, *J*=8.2 Hz), 7.52 (4H, *d*, *J*=8.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.6 (2C), 26.0 (2C), 29.1 (2C), 29.2 (4C), 29.3 (2C), 31.8 (8C), 68.0 (2C), 114.1 (4C), 128.4 (4C), 129.5 (4C), 160.2 (2C). HR FAB-MS: *m*/*z*, 639.4373 ($M+H^+$). Calcd for $C_{38}H_{58}N_2O_6$: M+H, 639.4373. E. A. Found: C, 71.45; H, 9.21; N, 4.35%, Calcd for $C_{38}H_{58}N_2O_6$: C, 71.44; H, 9.15; N, 4.38%.

**4B12** (72%), colorless crystals, m.p. 78-79°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.27-1.47 (36H, *m*), 1.78 (4H, *quint*, *J*=6.8 Hz), 3.57-3.87 (16H, *m*), 3.96 (4H, *t*, *J*=6.8 Hz), 6.87 (4H, *d*, *J*=8.2 Hz), 7.52 (4H, d, *J*=8.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.2 (2C), 29.3 (2C), 29.4 (2C), 29.56 (2C), 29.58 (2C), 29.61 (2C), 29.64 (4C), 31.9 (2C), 68.1 (8C), 114.1 (4C), 128.4 (4C), 129.5

(4C), 160.2 (2C). HR FAB-MS: *m/z*, 751.5624 ($M+H^+$). Calcd for $C_{46}H_{75}N_2O_6$: M+H, 751.5625. E. A. Found: C, 73.58; H, 10.00; N, 3.70%, Calcd for $C_{46}H_{75}N_2O_6$: C, 73.56; H, 9.93; N, 3.73%.

**4B16** (29%), colorless crystals, m.p. 89-90°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.26-1.46 (52H, *m*), 1.78 (4H, *quint*, *J*=6.8 Hz), 3.58-3.86 (16H, *m*), 3.96 (4H, *t*, *J*=6.8 Hz), 6.87 (4H, *d*, *J*=8.2 Hz), 7.52 (4H, *d*, *J*=8.2 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.2 (2C), 29.3 (4C), 29.4 (4C), 29.58 (4C), 29.61 (4C), 29.68 (6C), 31.9 (2C), 68.1 (8C), 114.1 (4C), 128.4 (4C), 129.5 (4C), 160.2 (2C). FAB-MS: *m/z*, 864 ($M+H^+$). E. A. Found: C, 75.07; H, 10.50; N, 3.26%, Calcd for $C_{54}H_{90}N_2O_6$: C, 75.13; H, 10.51; N, 3.24%.

### 2.2.6. Synthesis of *N,N'*-Bis(4-alkoxybenzoyl)-1,7-dioxa-4,10-diazacyclododecane (5B)

A thionyl chloride solution (0.5 $cm^3$) of 4-octyloxybenzoic acid (141.1 mg, 0.56 mmol) was refluxed for 3 h. After excess thionyl chloride was removed, a pyridine solution (3 $cm^3$) of 1,4,10,13-tetraoxa-7,16-diazacyclooctadecene (35.6 mg, 0.13 mmol) and a catalytic amount of DMAP was refluxed for 12 h, The reaction mixture was poured into $KHSO_4$ solution and extracted with ethyl acetate. After being dried on $MgSO_4$, the solvent was removed under reduced pressure. The residue was chromatographed on a silica-gel column using hexane and ethyl acetate as the eluent to give **5B_8** (92.9 mg, 98%) colorless crystals.

**5B8** (98%), colorless crystals, m.p. 75-76°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.89 (6H, *t*, *J*=6.8 Hz), 1.26-1.49 (20H, *m*), 1.78 (4H, *quint*, *J*=6.8 Hz), 3.61-3.76 (24H, *m*), 3.96 (4H, *t*, *J*=6.8 Hz), 6.87 (4H, *d*, *J*=8.7 Hz), 7.33 (4H, *d*, *J*=8.7 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.6 (2C), 26.0 (2C), 29.1 (2C), 29.2 (4C), 29.3 (2C), 31.8 (2C), 68.1 (4C), 69.9 (4C), 70.6 (4C), 114.2 (4C), 128.5 (4C), 128.6 (2C), 160.0 (2C), 172.1 (2C). FAB-MS: *m/z*, 727 ($M+H^+$). E. A. Found: C, 69.38; H, 9.13; N, 3.78%, Calcd for $C_{42}H_{66}N_2O_8$: C, 69.39; H, 9.15; N, 3.85%.

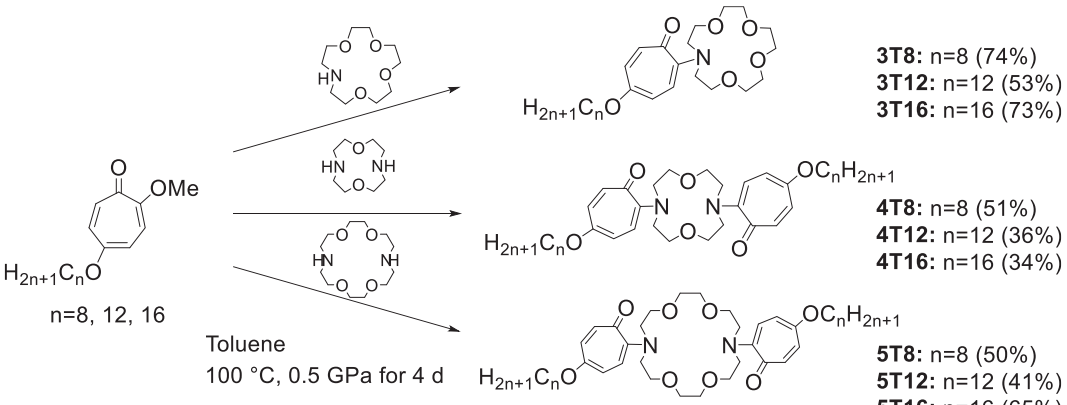
**5B16** (45%), colorless crystals, m.p. 96-97°C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$=0.88 (6H, *t*, *J*=6.8 Hz), 1.26-1.45 (52H, *m*), 1.78 (4H, *quint*, *J*=6.8 Hz), 3.61-3.76 (24H, *m*), 3.96 (4H, *t*, *J*=6.8 Hz), 6.87 (4H, *d*, *J*=8.7 Hz), 7.33 (4H, *d*, *J*=8.7 Hz). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$=14.1 (2C), 22.7 (2C), 26.0 (2C), 29.2 (2C), 29.3 (2C), 29.4 (4C), 29.56 (4C), 29.59 (4C), 29.65 (4C), 29.7 (4C), 31.9 (2C), 68.1 (4C), 69.8 (4C), 70.6 (4C), 114.2 (4C), 128.5 (4C), 128.5 (2C), 160.0 (2C), 172.1 (2C). FAB-MS: *m/z*, 952 ($M+H^+$). E. A. Found: C, 73.19; H, 10.38; N, 2.88%, Calcd for $C_{58}H_{98}N_2O_8$: C, 73.22; H, 10.38; N, 2.94%.

## 3. Result & Discussion

### 3.1. Synthesis

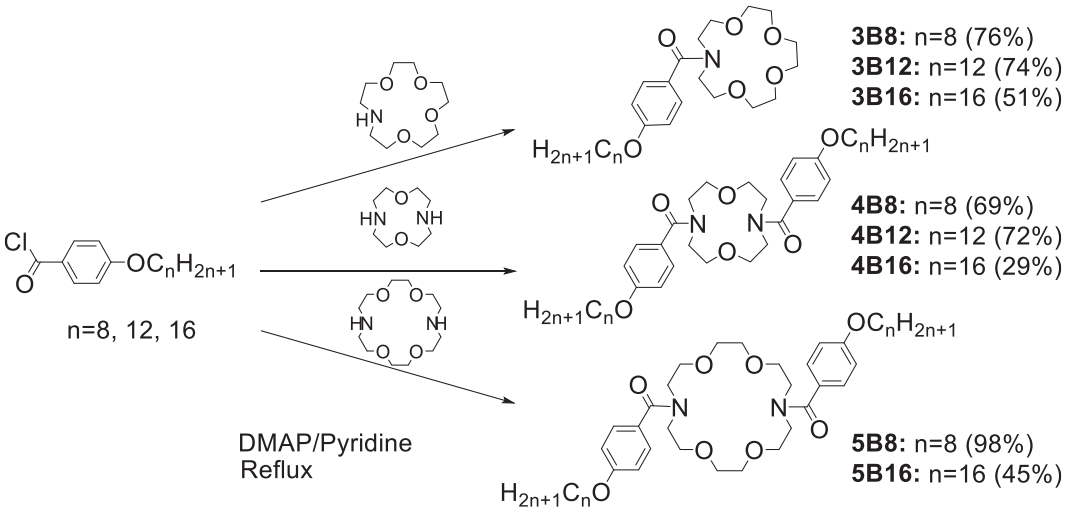
Troponoid azacrown ether derivatives (**3T**-**5T**) were synthesized via the condensation of 5-alkoxy-2-methoxytropone with the corresponding azacrown ethers (1-aza-15-crown-5, 4,10-diaza-

12-crown-4, and 4,13-diaza-18-crown-6) under high-pressure conditions (0.5 GPa) at 100°C for four days in toluene as shown in scheme 2. In contrast, the reaction did not proceed under ambient pressure, likely due to the reduced electrophilicity of 5-alkoxy-2-methoxytropone caused by the electron-donating alkoxy substituent at the C-5 position. The structure of *N,N*-bis(5-octyloxybenzene-2-yl)-diaza-12-crown-4 ether (**4T8**) was confirmed based on multiple spectroscopic and analytical techniques. The molecular ion peak at m/z 638 observed in the mass spectrum corresponds to the expected molecular weight of the target compound. In the $^{1}$H NMR spectrum, characteristic signals were detected for the diaza-12-crown-4 ether moiety [$\delta$=3.63 (16H, *s*)], the alkyl chains [$\delta$= 0.88 (6H, *t*, *J*=7.0 Hz), 1.27-1.45 (20H, *m*), 1.75 (4H, *quint*, *J*=7.0 Hz), 3.85 (4H, *t*, *J*=7.0 Hz)], and the aromatic rings [$\delta$=6.40 (2H, *d*, *J*=11.3 Hz), 6.97 (4H, *s*), 7.04 (2H, *d*, *J*=11.3 Hz)]. The $^{13}$C NMR spectrum further supported the proposed structure, showing signals at $\delta$= 14.1 (2C), 19.2 (2C), 31.0 (2C), 49.3 (2C), 68.1 (4C), 112.2 (2C), 122.0 (2C), 131.0 (2C), 135.6 (2C), 152.6 (2C), 157.6 (2C), and 181.5 (2C), consistent with the expected carbon environments. Elemental analysis results also matched the calculated values for the target compound, confirming its identity as **4T8**. The structures of related compounds (**3T-5T**) were similarly determined using these spectroscopic and analytical methods.




Scheme 2

The corresponding benzoyl derivatives (**3B-5B**) were obtained by reacting azacrown ethers (1-aza-15-crown-5, 4,10-diaza-12-crown-4, and 4,13-diaza-18-crown-6) with various 4-alkoxybenzoyl chlorides in pyridine, using a catalytic amount of DMAP, as shown in Scheme 3.




Scheme 3

### 3.2. Mesomorphic properties

Compounds **3T**-**5T** and **3B**-**5B** were examined using polarized optical microscopy. *N,N'*-Bis(5-alkoxytropon-2-yl)piperazine derivative (**1T**) and the 1,5,9-triazacyclododecane derivatives (**2T**) exhibited SmC and Cub phases, respectively. But the troponoid azacrown ether derivatives (**3T**-**5T**) and their benzoyl analogues (**3B**-**5B**) were not mesomorphic (Table 1).

Table 1. Transition temperatures of **3T**-**5T** and **3B**-**5B**

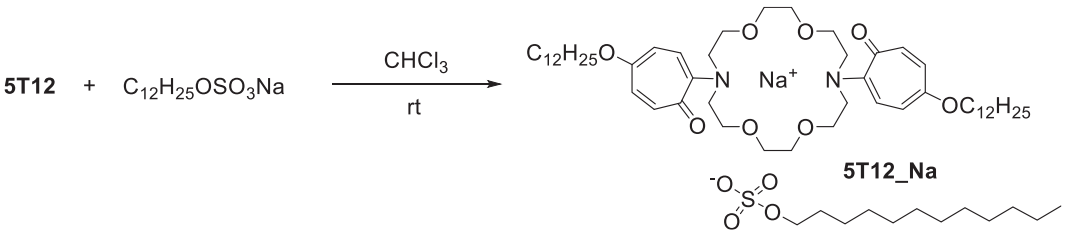
| Compounds | n | Transition temperature/°C | Compounds | n | Transition temperature/°C |
|---|---|---|---|---|---|
| **3T8** | 8 | yellow oil | **3B8** | 8 | colorless oil |
| **3T12** | 12 | Cr·122·Iso | **3B12** | 12 | colorless oil |
| **3T16** | 16 | Cr·70·Iso | **3B16** | 16 | Cr·59·Iso |
| **4T8** | 8 | Cr·101·Iso | **4B8** | 8 | Cr·69·Iso |
| **4T12** | 12 | Cr·106·Iso | **4B12** | 12 | Cr·79·Iso |
| **4T16** | 16 | Cr·102·Iso | **4B16** | 16 | Cr·90·Iso |
| **5T8** | 8 | Cr·67·Iso | **5B8** | 8 | Cr·76·Iso |
| **5T12** | 12 | Cr·77·Iso | **5B12** | 12 | Cr·87·Iso[10] |
| **5T16** | 16 | Cr·87·Iso | **5B16** | 16 | Cr·97·Iso |

Interestingly, when comparing benzenoid crown ether derivatives with identical alkyl chain lengths, compound **5T**—featuring the larger diaza-18-crown-6 ring—exhibited a lower melting point than its smaller-ring counterpart, **4T**. This observation suggests that the size of the azacrown ether ring influences thermal properties, likely by affecting molecular packing behavior.

Furthermore, the nature of the central core plays a critical role in mesophase formation. Azacrown ethers are known for their high conformational flexibility, attributed to multiple rotatable bonds and their macrocyclic architecture.[25] Such flexibility likely hinders the adoption of a well-ordered, anisotropic arrangement necessary for liquid crystalline phase formation. In contrast, the relatively rigid piperazine core in compound **1T** may promote molecular alignment into layered structures, thereby facilitating mesophase behavior. The melting points of the troponoid derivatives (**3T**, **4T**) were higher than those of the corresponding benzene derivatives (**3B**, **4B**), indicating that the tropone ring—characterized by a significant dipole moment—enhances intermolecular interactions and molecular rigidity. This, in turn, raises the melting point and suppresses liquid crystalline phase formation. In both troponoid (**3T**-**5T**) and benzene (**3B**-**5B**) derivatives, azacrown ethers serve as linkers between monocyclic benzoyl or benzene rings. This structural configuration appears to yield an unfavorable balance between rigidity and flexibility, which is essential for the development of ordered mesophases. As a result, these compounds did not exhibit mesomorphic behavior.

In the study of liquid crystalline compounds incorporating crown ethers, several attempts have been made to utilize the complexation ability of crown ethers to control molecular orientation. Previous studies have demonstrated that *N,N'*-di(tropon-2-yl)-diaza-18-crown-6 ether readily forms stable complexes with sodium ion, highlighting its potential as a selective ion-binding ligand. Based on this observation, we synthesized sodium and silver complexes of **5T12** to evaluate their mesomorphic properties, considering the known affinity of troponoid systems for silver ions.

To prepare the sodium complex (**5T12_Na**), equimolar amounts of diaza-18-crown-6 ether (**5T12**) and sodium dodecyl sulfate were stirred in chloroform at room temperature for one day. After solvent removal, the sodium salt complex (**5T12_Na**) was obtained (scheme 4). Its structure was confirmed by mass spectrometry, showing a molecular ion peak at *m/z* 1126, consistent with the expected molecular weight. In the $^{1}$H NMR spectrum, in addition to the signals from **5T12**, new peaks corresponding to the sodium dodecyl sulfate moiety were observed [$\delta$=0.88 (3H, *t*, *J*=6.7 Hz), 1.27-1.45 (17H, *m*), 1.64-1.81 (3H, *m*), 4.06 (2H, *t*, *J*=6.7 Hz)]. Notably, the proton signals from the crown ether shifted upfield and those from the tropone ring shifted downfield, accompanied by broadening, indicating successful complexation. The silver dodecyl sulfate complex of the 4,13-diaza-18-crown-6 derivative (**5T12_Ag**) was synthesized analogously and structurally characterized.




Scheme 4

Polarized optical microscopy of **5T12_Na** revealed no distinct optical textures during cooling; however, upon applying pressure to the sample, a soft intermediate phase was observed (Fig. 1).

Fig. 1. Texture of mesophase of **5T12_Na** at 36°C obtained on cooling from the isotropic liquid.

Differential scanning calorimetry (DSC) measurements of **5T12_Na** showed peaks at 60.4°C and 62.0°C during the cooling process, suggesting that compound (**5T12_Na**) exhibits a monotropic mesophase. Although X-ray diffraction was attempted to elucidate the packing model of this phase, no reflections were detected, likely due to the low degree of order. These results indicate that the formation of a sodium complex with the otherwise non-liquid crystalline compound (**5T12**) induces liquid crystalline behavior. This is attributed to the fixation of the flexible crown ether moiety upon complexation, effectively enlarging the rigid core and promoting mesophase formation. In contrast, the silver complex (**5T12_Ag**) was not mesomorphic (Cr・45・Iso). This suggests that the nature of the metal cation plays a critical role in mesophase induction.

In conclusion, troponoid azacrown ether derivatives (**3T-5T**) bearing long alkyl chains were successfully synthesized via the reaction of 5-alkoxy-2-methoxytropone with various azacrown

ethers, including 1-aza-15-crown-5, 4,10-diaza-12-crown-4, and 4,13-diaza-18-crown-6, under high-pressure conditions. Among these, the 4,13-diaza-18-crown-6 derivative (**5T12**) was found to form stable complexes with sodium dodecyl sulfate and silver dodecyl sulfate. Although the troponoid azacrown ether derivatives (**3T**-**5T**) and the corresponding benzenoid derivatives (**3B**-**5B**) themselves did not exhibit liquid crystalline properties, the complexation of **5T12** with sodium dodecyl sulfate induced a monotropic mesophase, revealing its potential for supramolecular liquid crystalline behavior. These crown ethers bearing long alkyl chains are expected to find applications in a wide range of fields, including metal ion extraction, liquid membrane transport, surfactant systems, and liquid crystals.

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