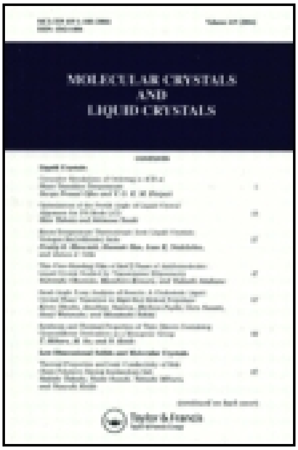

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Synthesis and Properties of Cholesteric Liquid Crystal Crown Ethers

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Synthesis and Properties of Cholesteric Liquid Crystal Crown Ethers

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Five cholesteric liquid crystal crown ethers were synthesized by treating 4′-aminobenzo-15-crown-5, cis(trans)-4.4′-diaminodibenzo-18-crown-6 with cholesteryl chlorocarbonate and cholesteryl chloroacetate respectively. Their structure had been elucidated with Elementary Analysis, IR, ^{1}HNMR and MS, and their properties relevant to cholesteric liquid crystal were determined by using DSC and Texture. The complex constant of the liquid crystal crown ethers with potassium perchlorate were determined also. The effects of doping inorganic salts to the clear point were studied. The changes of the transition temperatures between the two isomeric liquid crystal crown ethers (cis-isomer and trans-isomer) and that of their mixture were likewise determined.

Keywords: cholesteric liquid crystal, crown ethers, doping

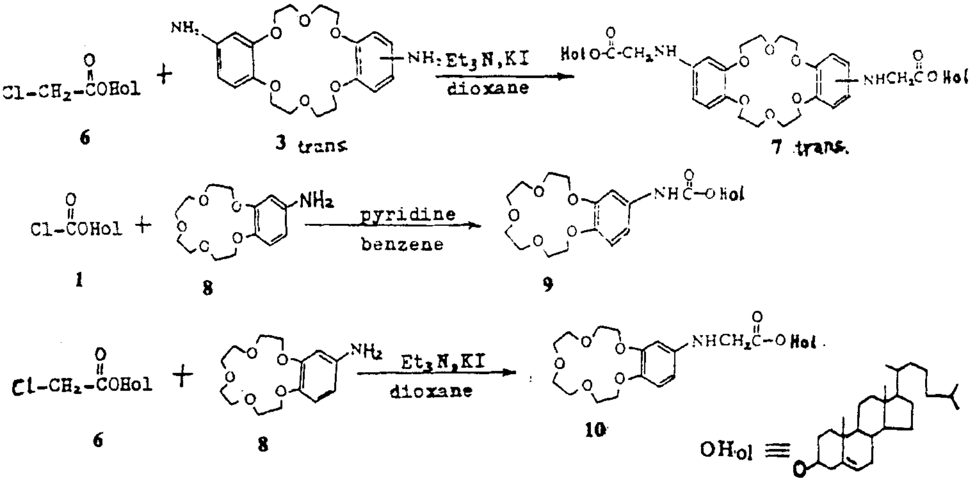
Since electroconducting cholesteric mesomorphic crown ethers was for the first time reported by Bogatskaya *et al.*[1] in 1982, nematic,[2–6] dish,[7–8] polymer[9–12] liquid crystal crown ethers subsequently described one after another. Lehn[13] held that molecular ionic devices could be established with crown ethers. Being stimulated by the pioneering work, we attempted to synthesize five cholesteric liquid crystal crown-ethers with diversified type. Their properties of doping inorganic salts had been studied.

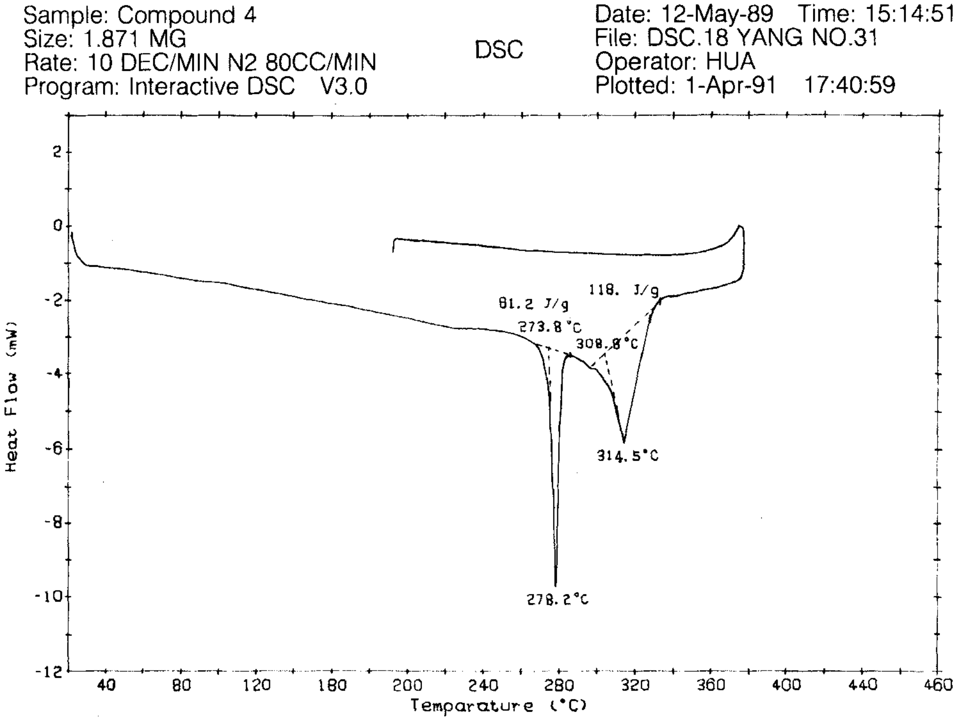
Scheme of synthesis:

1

2.Cis,
3.trans,

4.Cis,
5.trans,



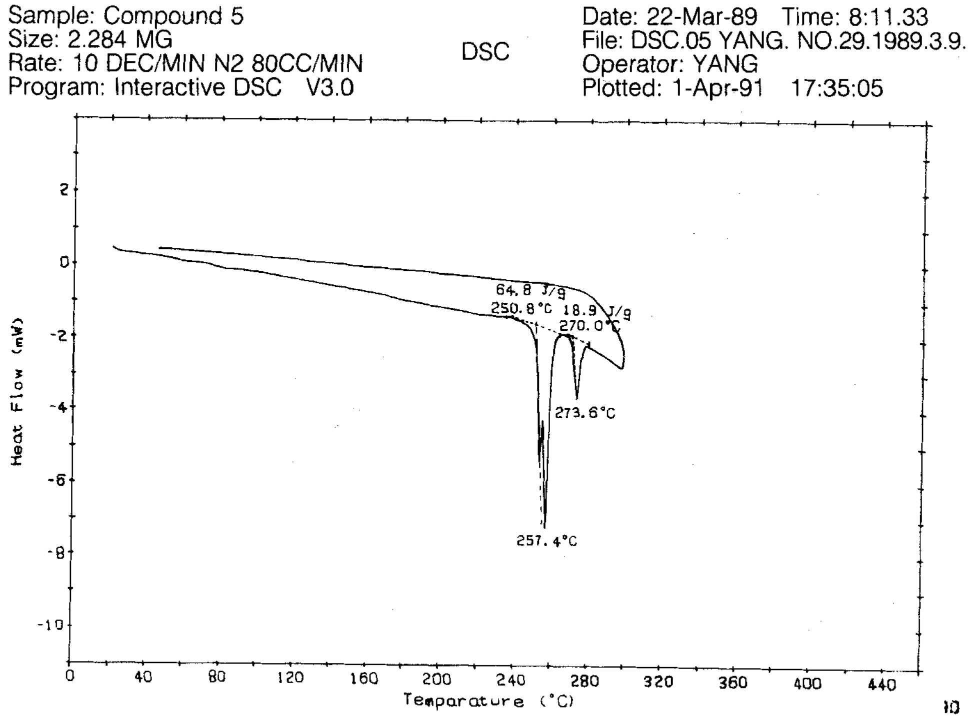


Sample: Compound 4
Size: 1.871 MG
Rate: 10 DEC/MIN N2 80CC/MIN
Program: Interactive DSC V3.0

DSC

Date: 12-May-89 Time: 15:14:51
File: DSC.18 YANG NO.31
Operator: HUA
Plotted: 1-Apr-91 17:40:59

FIGURE 1 DSC of compound **4**.

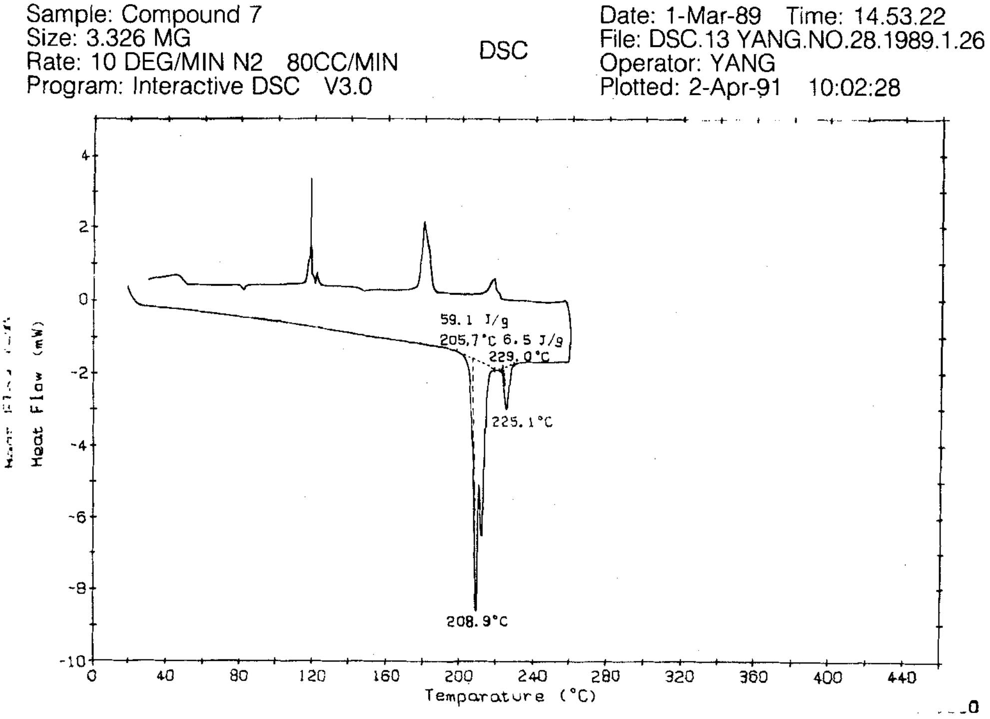


Sample: Compound 5
Size: 2.284 MG
Rate: 10 DEC/MIN N2 80CC/MIN
Program: Interactive DSC V3.0

DSC

Date: 22-Mar-89 Time: 8:11.33
File: DSC.05 YANG. NO.29.1989.3.9.
Operator: YANG
Plotted: 1-Apr-91 17:35:05

FIGURE 2 DSC of compound **5**.



Sample: Compound 7
Size: 3.326 MG
Rate: 10 DEG/MIN N2 80CC/MIN
Program: Interactive DSC V3.0

DSC

Date: 1-Mar-89 Time: 14.53.22
File: DSC.13 YANG.NO.28.1989.1.26
Operator: YANG
Plotted: 2-Apr-91 10:02:28

FIGURE 3 DSC of compound **7**.

FIGURE 4 Texture of compound **4**(240°C, on cooling). See Color Plate IV.

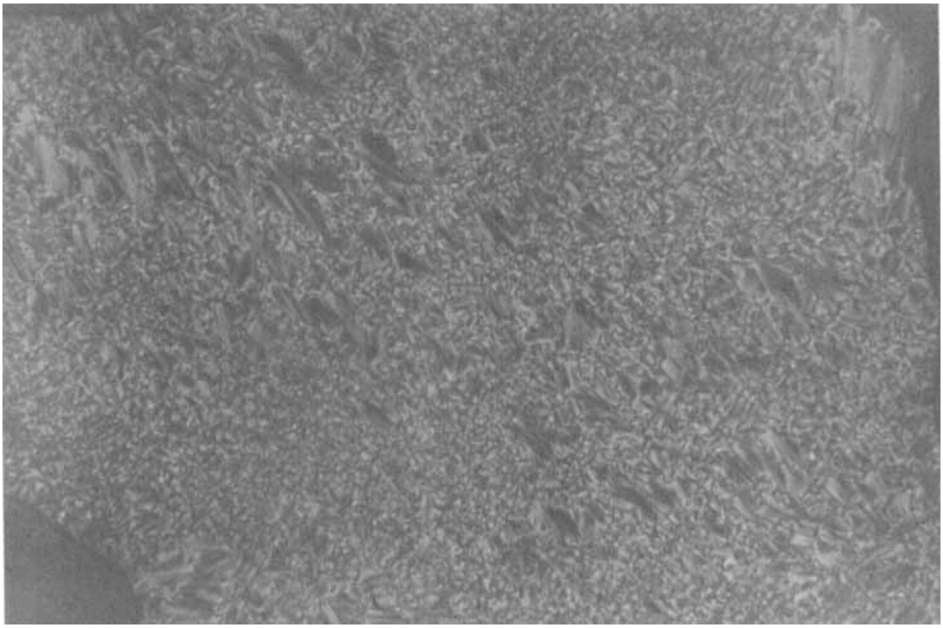


FIGURE 5 Texture of compound **5**(235°C, on cooling). See Color Plate V.

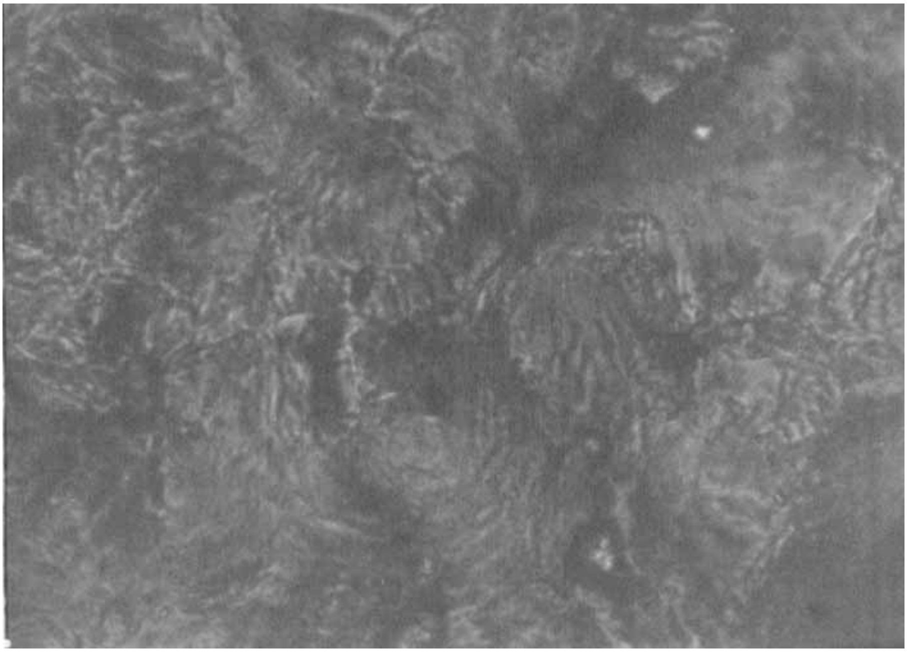


FIGURE 6 Texture of compound **7**(220°C, on cooling). See Color Plate VI.

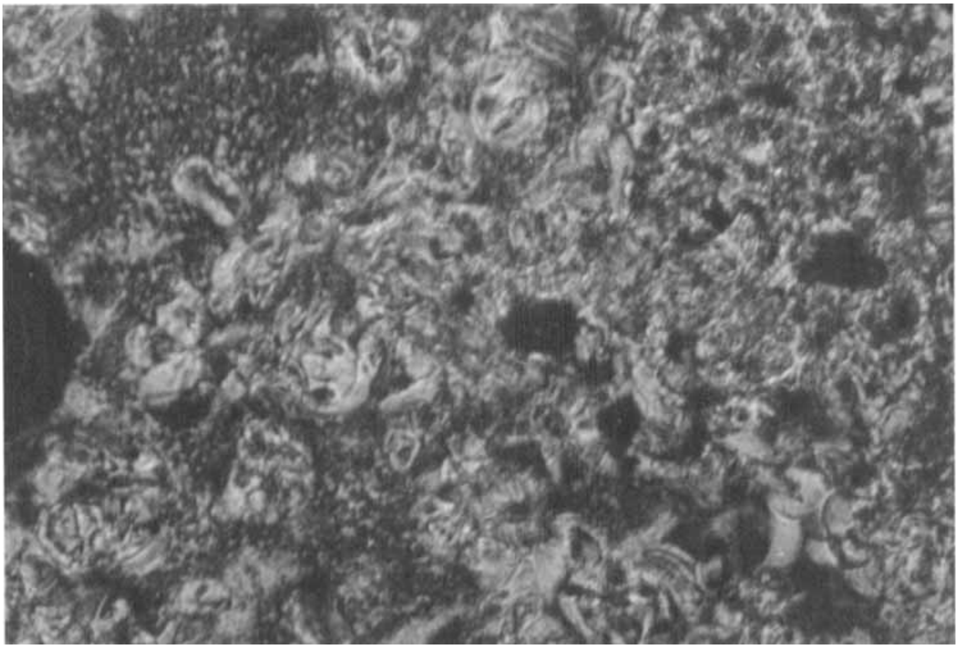


FIGURE 7 Texture of compound **9**(130°C, on cooling). See Color Plate VII.

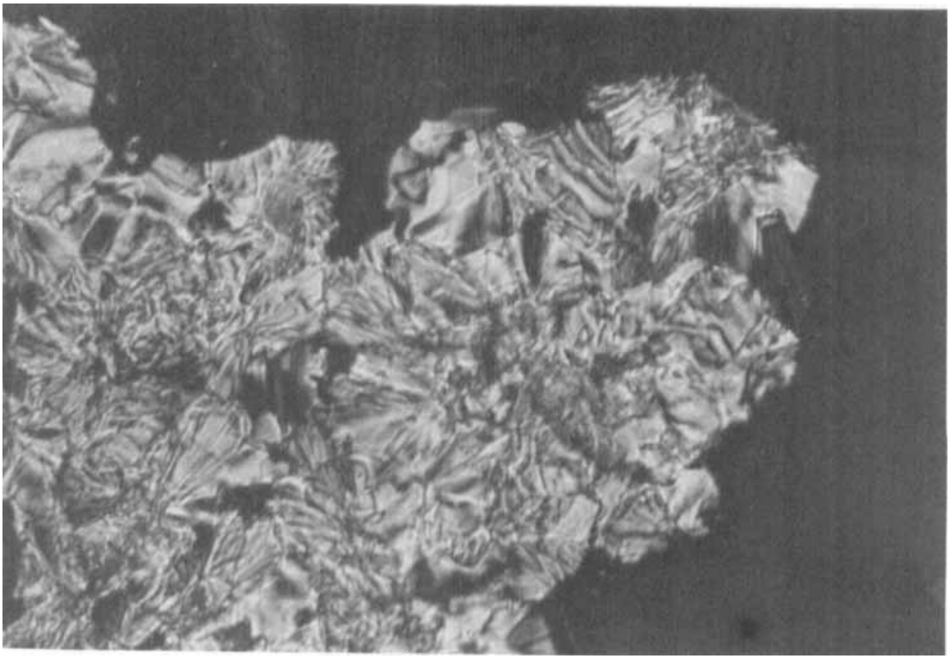


FIGURE 8 Texture of compound **10**(90°C, on cooling). See Color Plate VIII.

RESULTS AND DISCUSSION

Crown ethers **4**, **5**, **7**, **9**, **10** showed properties of cholesteric liquid crystal by DSC and texture determination respectively.

The complexes composed of the liquid crystal crown ethers with potassium ion were determined by conductance and spectrophotometric method. See Table I.

In Table I it is shown that the complexes of **4**, **5**, and **9** with K^+ are 1:1 type (mole proportion). Hole size of 18-crown-6 (2.6–3.2 Å) is larger than 15-crown-5 (1.7–2.2 Å) and fit well to the size of K^+ (diameter 2.66 Å), so that complex stability of **4** and **5** with K^+ is stronger than **9**. Complex constant of trans-isomer (**5**) with K^+ increases, since the steric hindrance effect therein is smaller than the cis-isomer (**4**).

Effect of doping inorganic salt on the properties of liquid crystal crown ethers.

Method of doping: The crown ether and potassium thiocyanate are dissolved in acetone, chloroform or methanol. At room temperature the solvent is evaporated at reduced pressure resulting in a molten residue which solidified upon cooling. The doped liquid crystal crown ethers thus obtained are measured with DSC and texture.

It has been shown that **7** doped KSCN possess, none the less, the properties of

TABLE I

Complex constant (Kf) of liquid crystal crown ethers at 25 ± 0.01°C

crown ether ligand	Inorganic salt	log Kf *)	composition proportion of complex ligand: inorganic salt
9	$KClO_4$	4.85	1:1
4	$KClO_4$	5.55	1:1
5	$KClO_4$	5.77	1:1

*) **5**. **9** used $CHCl_3$–CH_3CN (1:1 V / V) as solvent;

4 used $CHCl_3$–CH_3CN (3:2 V / V) as solvent.

liquid crystal of which the melting point decreases and the clear point increases as the content of **7** increases. See Figure 9 and Table II.

Compounds **4** and **5** were doped with KSCN in the same way there result in some specimen with properties of liquid crystal. These are shown in Table III and Table IV. The clear point of **4** decrease, and the clear point of **5** increase as the content of KSCN increase. The effect of doping KSCN on clear point for **5** was similar to that of **7**, implying that both **5** and **7** were trans-isomer of liquid crystal crown ethers.

Cis-isomer (**4**) and trans-isomer (**5**) of liquid crystal crown ether (mol ratio 1:1) were dissolved in $CHCl_3$. By removing all the solvent, a molten residue which solidied upon cooling was obtained. Determination of DSC and texture show that the mixture of cis- and trans-isomer still display the properties of liquid crystal, T_{KC} 230°C T_{CI} 260°C, the melting point and clear point being lower than that of the cis or trans-isomer. Presumably cis and trans-isomers were still in admixture giving mixture crown ether liquid crystal with low melting point.

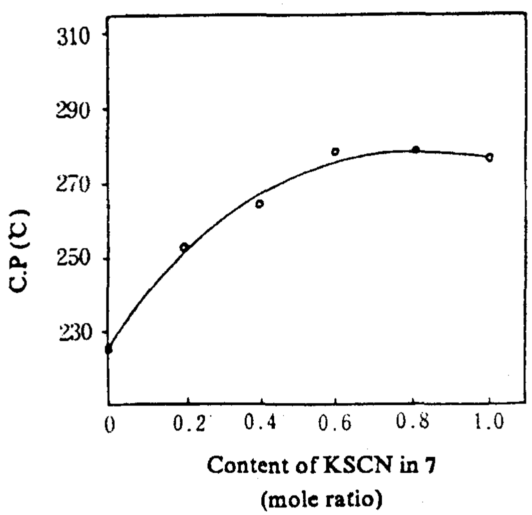


FIGURE 9 The effect of content of doping KSCN in compound **7** on the clear point (c.p).

TABLE II

Transition temperature of **7** doped KSCN

7:KSCN (mole ratio)	Transition temperature (℃)
1 : 0	$K \xrightarrow{208.9} M \xrightarrow{212} Ch \xrightarrow{225.1} Cp$
1 : 0.2	$K \xrightarrow{194} M \xrightarrow{226} Ch \xrightarrow{252} Cp$
1 : 0.4	$K \xrightarrow{194} M \xrightarrow{226} Ch \xrightarrow{276} Cp$
1 : 0.6	$K \xrightarrow{194} M \xrightarrow{226} Ch \xrightarrow{278} Cp$
1 : 0.8	$K \xrightarrow{194} M \xrightarrow{226} Ch \xrightarrow{278} Cp$
1 : 1.0	$K \xrightarrow{190} M \xrightarrow{226} Ch \xrightarrow{278} Cp$

TABLE III

Transition Temperature of **4** doped KSCN (°C)

4:KSCN (mole ratio)	Transition temperature (℃)
1 : 0	$K \xrightarrow{278} Ch \xrightarrow{314.5} Cp$
1 : 0.2	$K \xrightarrow{268} M \xrightarrow{280} Ch \xrightarrow{288} Cp$
1 : 0.4	$K \xrightarrow{266} M \xrightarrow{280} Ch \xrightarrow{309} Cp$
1 : 0.6	$K \xrightarrow{260} M \xrightarrow{284} Ch \xrightarrow{308} Cp$

TABLE IV

Transition temperature of 5 doped KSCN (°C)

5:KSCN (mole ratio)	Transition temperature (℃)
1 : 0	$K \xrightarrow{257.4} Ch \xrightarrow{273.6} Cp$
1 : 0.2	$K \xrightarrow{244} M \xrightarrow{284} Ch \xrightarrow{295} Cp$
1 : 0.4	$K \xrightarrow{241} M \xrightarrow{284} Ch \xrightarrow{298} Cp$
1 : 0.6	$K \xrightarrow{234} M \xrightarrow{265} Ch \xrightarrow{297} Cp$

EXPERIMENTAL

Instrument: Infrared (IR) spectra were recorded on Nicolet ET-IR 170SX as neat films on KBr plates. Proton nuclear magnetic resonance spectra (^{1}HNMR) were recorded on JNM-FX90Q spectrometer in $CDCl_3$ solvent. Mass spectrometry (MS) were carried out on Finnigan-Mat 4510 GS-MS and Hitach M-80 A GS-MS (FD). Element Analysis were obtained on Carlo Erba 1106. Differential scanning calorimeter (DSC) were recorded on Dupont 1090 Thermal Analysis. Texture were taken on XPT-7 Microscope with polariscope made in Jiang-nan Optical Instrument Factory (with the attachment of a heat plate which was produced by Scientific Instrument Plate of Sichuan University).

The Synthesis of Intermediates and Products

Intermediates **1**, **2**, **3**, **6**, **8** were synthesized respectively by method of [**14**], [**15**], [**16**], [**17**], [**18**]. **1** yield 78.7%, m.p. 120–122°C (lit.[14] 122–3.5°C); **2** yield 80%, m.p. 177–8°C (lit.[15] 177–8°C); **3** yield 93%, m.p. 194–7°C (lit.[16] 196–200°C); **6** yield 67.3%, m.p. 157–9°C (lit[17] 156–9°C); **8** yield 90%, m.p. 72–4°C (lit.[18] 73–4°C).

Compound 4: compound **1**(2.42 g, 5.40×10^{-3} mol) was dissolved in anhydrous dioxane (20 mL) in a three-necked, round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, a nitrogen inlet and a dropping funnel, anhydrous pyridine (0.4 mL) was then added and the mixture was heated. When the solution begin to reflux, **2**(1.00 g, 2.56×10^{-3} mol) in anhydrous dioxane (40 mL) was added to the reaction mixture over 10 minutes via the dropping funnel. After additions were complete, the mixture was stirred and refluxed for an additional 1.3 h. The reaction mixture was filtered and cooled. White solid (0.75 g. yield 24%) was obtained as the product by filtration. The product was recrystallized from chloroform-acetone to give white crystal (0.37 g). T_{KC} 278.2°C, T_{CI} 314.5°C. Anal. calcd for $C_{76}H_{114}N_2O_{10}$: C, 75.12; H, 9.39; N, 2.31. Found: C, 75.01; H, 9.43; N, 2.20. IR (cm^{-1}): 3354 (m, NH), 1728 (m, C═O) 1586, 1505 (s, Ar), 1263, 1216, 1136 (s, C—O—C), ^{1}HNMR (ppm): 7.16–6.47 (6H, m, 2 × [Ar-H]$_3$), 5.42 (2H, s, 2 × C═CH), 4.57 (2H, s, 2 × NH), 4.12–4.00 (16H, m, 8 × OCH_2), 2.41–0.68 (88H, m, cholesteryl ring), m/z (FDMS): 1215 ($[M + H]^+$, 27%), 828 (60), 368 (100).

Compound 5: compound **1** (1.0 g, 2.56×10^{-3} mol), anhydrous dioxane (25 mL) and anhydrous pyridine (0.42 mL) were mixed in a three-necked round-bottomed flask equipped with a mechanical stirrer, a reflux condenser, a nitrogen inlet and a dropping funnel. The reaction mixture was heated under nitrogen atmosphere till refluxing set in, then the solution of compound **3** (2.56 g, 5.71×10^{-3} mol) in anhydrous dioxane (25 mL) was added to the reaction flask over 7 minut. After addition was complete, the mixture was stirred and refluxed for an additional 1.5 h. The reaction mixture was filtered. The filtrate was poured in the water (25 mL), when was filtrated and evaporated to dryness. White solid (2.61 g) product was obtained. The crude product was recrystallized from chloroform-anhydrous ethanol to give white powder. T_{KC} 257.4°C T_{CI} 273.6°C Anal. calcd for $C_{76}H_{114}N_2O_{10}$: C, 75.12; H, 9.39; N, 2.31. Found: C, 75.38; H, 9.35; N, 2.22, IR (cm^{-1}): 3332, 3444 (m, NH), 1731 (s, C═O), 1606, 1511 (s, Ar), 1260, 1221, 1133 (s, C—O—C). ^{1}HMNR (ppm): 7.16–6.45 (6H, m, 2 × $[Ar\text{-}H]_3$), 5.41 (2H, s, 2 × C═CH), 4.55 (2H, s, 2NH), 4.11–4.00 (16H, m, 8 × OCH_2), 2.41–0.68 (88H, m, cholesteryl ring). m/z (FDMS): 1215 ($[M + H]^+$, 100%), 829 (8).

Compound 7: compound **6** (4.98 g, 1.08×10^{-2} mol), anhydrous dioxane (100 mL), KI (0.4 g), triethyl amine (2 mL) and compound **3** (2 g, 5.13×10^{-3} mol) were mixed in three-necked round-bottomed flask, under nitrogen atmosphere. The reaction mixture was stirred, and refluxed for 40 h under nitrogen atmosphere. The reaction mixture was then stood and cooled. The solid was separated by filtration. Pink solid (2.26 g) was obtained. The crude product was recrystallized from chloroform-95% ethanol to give white flake crystal (1.08 g). T_{KM} *208.9°C T_{MC} 212.0°C T_{CI} 225.1°C. Anal. calcd for $C_{78}H_{118}N_2O_{10}$: C, 75.36; H, 9.50; N, 2.25. Found: C, 75.57; H, 9.77; N, 2.24. IR (cm^{-1}): 3410 (m, NH), 1735 (m, C═O), 1618, 1510 (m, Ar), 1265, 1214, 1135 (s, C—O—C). ^{1}HNMR (ppm): 6.83–6.11 (6H, m, 2 × $[Ar\text{-}H]_3$), 5.40 (2H, s, 2 × C═CH), 4.68 (2H, s, 2 × NH), 4.08–3.84 (20H, m, 8 × OCH_2, 2 × $COCH_2$), 2.38–0.68 (88H, m, cholesteryl ring). m/z (FDMS): 1343 ($[M + H]^+$, 100%), 817(13).

Compound 9: compound **1** (1.7 g, 3.79×10^{-3} mol) and benzene (30 mL) were mixed in three-necked round-bottomed flask. The mixture was stirred, and refluxed under nitrogen atmosphere, when the solutions of compound **8** (1.0 g, 3.53×10^{-3} mol) and pyridine (0.5 mL) in benzene (20 mL) were added for 30 min. The refluxing and stirring were continued for an additional 30 minutes. The mixture was filtered, the filtrate was vacuum distilled to remove solvent to give red oil which oil was taken with 95% ethanal. The white solid separated upon cooling was taken as the crude product which was chromatographed (silica gel G, chloroform/acetone/methanol, volume ratio 5/5/1), then recrystallized from benzene-light petroleum to give rod crystal. T_{KI} 178.2°C T_{IC} 135.5°C. Anal. calcd for $C_{42}H_{65}NO_7$: C, 75.52; H, 9.35; N, 2.01. Found: C, 75.64; H, 9.42; N, 1.97. IR (cm^{-1}): 3420 (m, NH), 1732 (m, C═O), 1610, 1515 (s, Ar), 1262, 1221, 1135 (s, C—O—C), ^{1}HNMR (ppm): 6.77–6.47 (3H, m, $[Ar\text{-}H]_3$), 5.43 (1H, s, C═CH), 4.57 (1H, s, NH) 4.11–3.75 (16H, m, 8 × OCH_2), 2.41–0.68 (44H, m, cholesteryl ring). m/z, 696 ($[M + H]^+$, 14%), 387 (78), 327 (41), 309 (72), 177 (100).

Compound 10: compound **8** (2.21 g, 7.81×10^{-3} mol), Compound **6** (3.61 g, 7.81×10^{-3} mol), KI (0.4 g) triethyl amine (1 mL) and dioxane (70 mL) were mixed in three-necked round-bottomed flask. Under N_2 atmosphere the mixture was stirred and refluxed for 17 h, then filtered. The filtrate was vacuum distilled to remove solvent to give red oil, which was chromatographed (silica gel G, chloroform/acetone/methanol, volume ratio 5/5/1), then recrystallized from 95% ethanol to give white powder. T_{KI} 134.2°C T_{IC} 90°C. Anal. calcd for $C_{43}H_{67}NO_7$: C, 72.78; H, 9.45; N, 1.97. Found: C, 72.95; H, 9.31; N, 1.92. IR (cm^{-1}): 3427 (m, NH), 1736 (s, C═O), 1615, 1510 (m, Ar), 1267, 1206, 1134 (s, C—O—C). ^{1}HNMR

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* T_{KM}: temperature of transition from solid state to mesomorphic state.

(ppm): 6.84–6.20 (3H, m, $[Ar\text{-}H]_3$), 5.39 (1H, s, C═CH), 4.70 (1H, s, NH), 4.07–3.75 (18H, m, 8 × OCH_2, $COCH_2$), 2.38–0.68 (44H, m, cholesteryl ring) m/z. 710 ($[M + H]^+$, 6.5%), 369 (70), 164 (84), 45(100).

CONCLUSION

Five crown ethers (**4**, **5**, **7**, **9**, **10**) were synthesized by treating 4′-aminobenzo-15-crown-5, cis(trans)-4,4′-diaminobenzo-18-crown-6 with cholesteryl chlorocarbonate and cholesteryl chloroacetate respectively. They showed properties of cholesteric liquid crystal and complexing properties with K^+. The five cholesteric liquid crystal crown ethers doped KSCN also possessed properties of cholesteric liquid crystal. The effect of doping KSCN on clear points for the trans-isomer (**5**, **7**) was similar: the clear points of **5**, **7** doped KSCN increased as the content of KSCN increased. The mixture of cis- and trans-isomer (**4**, **5**) showed still properties of cholesteric liquid crystal.

Acknowledgment

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