The thermal and optical properties of the liquid crystals doped by the picrates were examined by use of the micromelting point apparatus equipped with a polarizer. Figure 2 gives the effect of picrate doping on the clearing points (T_{NI}) of **5c**.

UV spectra of the picrate-doped liquid crystals containing a crown ether unit were measured by a multichannel spectrophotometer (Otsuka Electronics, MCPD-100) using a heated sample holder as shown in Figure 4. The sample cell is composed of two quartz plates and aluminum foil spacers (thickness 30–40 nm). The sample in the cell was heated to an isotropic state once before the measurement. The thickness of the sample was determined by a light interference method commonly used for thin film or thin IR cells with the same instrument in the melt state. The sample thickness thus obtained is in the range 50–80 nm. Figure 3 shows examples of the UV spectra, and Table V gives a list of λ_{max} values for the UV spectra in the liquid-crystalline state or in the isotropic state.

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Fluorescence and Absorption Studies of the Cation-Binding Behavior of "Crowned" Liquid Crystals in Solution and in the Nematic Phase

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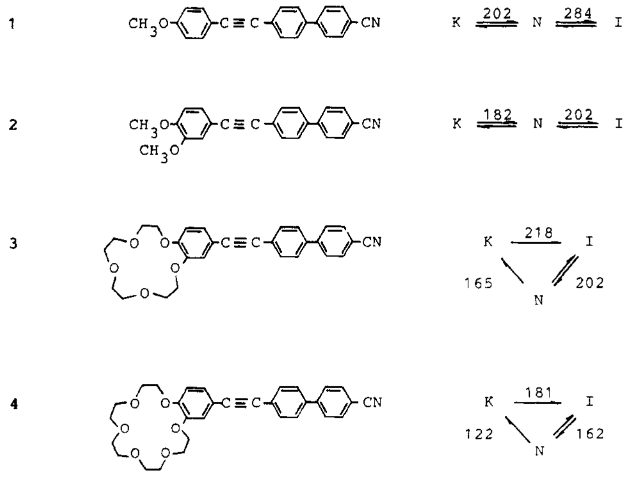
4′-((*p*′-Cyanobiphenylyl)ethynyl)benzo crown ethers (**3** and **4**) not only display a nematic liquid-crystal phase but also show very strong fluorescence, both in solution and in the liquid-crystalline state. The "crowned" liquid crystal compound **4** exhibited a bathochromic shift in fluorescence and a hypsochromic shift in absorption with increasing solvent polarity. The addition of alkali-metal cations produced hypsochromic changes in both the fluorescence and absorption of **4**. The cation-induced effects (fluorescence, absorption, and fluorescence quenching with thiocyanate salts) have been used as aids in determining the cation-binding ability of **4** in polar solvents, producing results similar to those obtained from conventional methods. On the basis of solution studies, the binding abilities of **3** and **4** in a eutectic nematic liquid crystal (ZLI-2806) were determined. The results revealed that **3** and **4** also complex alkali-metal cations selectively in the nematic phase, and the cation-binding ability is comparable with that found in methanol solution, but no evidence for 2:1 crown unit:cation complexation of **3** with KSCN was obtained under the present conditions. On the other hand, an energy-transfer quenching study with sodium 3-perylenecarboxylate under the same conditions did not show any specific cation–crown ether interaction.

The absorption and fluorescence properties of crown ether compounds have been studied extensively, and many compounds referred to as "chromoionophores" or "fluoroionophores" have been synthesized.[1] Because of their high sensitivity and selectivity, fluoroionophores are often considered to be exceptionally convenient for the study of ion-binding behavior. For example, the phenolic fluoroionophores with umbelliferone units[2] and benzothiazolylphenols bearing a crown ether unit[3] are used in fluorometric determination of alkali- and alkaline-earth-metal cations in solutions. The anthracenoyl crown ethers have been used as fluorescent probes for the solid-phase transition of phosphatidylcholine,[4] and the diastereomeric complexation behavior of the chiral coronands was studied by means of their quenching phenomena.[5]

In previous papers we reported the syntheses and thermal properties of new liquid-crystalline compounds bearing a crown ether ring and demonstrated that the selective cation binding of crown ethers could also be observed in the liquid-crystalline state by a picrate doping experiment.[6] We also found that 4′-((p′-cyanobiphenylyl)ethynyl)benzo crown ethers (**3** and **4** in Chart I) not only display a nematic liquid crystal phase but also show a very strong fluorescence both in solutions and in the liquid-crystalline state.

The complexation behavior of various crown ethers has been observed primarily in solution; there are also many studies on the solid-state structure of crown ether complexes. Recently the binding behavior of crown ethers in

Chart I[a]



[a] Transition temperature in °C. K, N, and I represent crystal, nematic, and isotropic phase, respectively.

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Scheme I

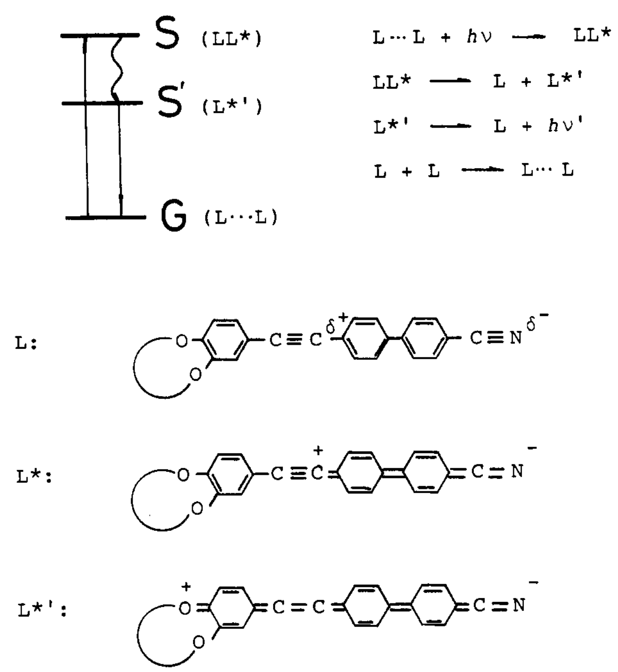

Table I. Absorption and Fluorescence Properties of Compounds 1-4 in MeOH at 25 °C (Excitation 330 nm)

	absorption		fluorescence	
compd	λ_{max}, nm	ϵ_0	λ_{max}, nm	Φ_0
1	319	53 000	428	*a*
2	325	49 000	467	*a*
3	324	49 000	468	*a*
4	324	37 000	467	0.33

[a] Not determined.

interfacial circumstances was studied by Matsumura et al.,[7] and Izatt et al. determined the cation-binding ability of silica-gel-bound crown ethers.[8] Concerning the cation-binding behavior of crown ether compounds in the liquid-crystal state, however, almost nothing is known, although such investigations would have ramifications for both material science and coordination chemistry. In this paper, the results of a detailed study of the cation-binding properties of the new fluoroionophores 3 and 4 in solution are presented. The binding abilities of these two compounds in the nematic phase were also determined by a fluorescence-quenching method.

Results and Discussion

Basic Spectral Features and Cation-Binding Effects. In methanol the fluoroionophore 4 shows an absorption and a fluorescence at λ_{max} = 324 nm and λ_{max} = 467 nm, respectively (Figure 1). The large difference between the absorption and fluorescence maxima reveals that the two singlet excited states (S and S' in Scheme I) differ considerably in their electronic states. As seen in Table I, the absorption and fluorescence spectra of the "crowned" liquid crystals 3 and 4 are almost the same as those of the dimethoxy analogue 2. The solvent effect on the absorption and fluorescence of 4 is noticeable, as shown in Table II. A polar solvent results in a large bathochromic shift in the fluorescence of 4, which is consistent with the behavior seen in π–π^* transitions, but in the absorption spectrum an increase in solvent polarity produces a small hypsochromic shift, indicative of an n–π^* transition.[9] Figure 2 depicts the changes in the emission

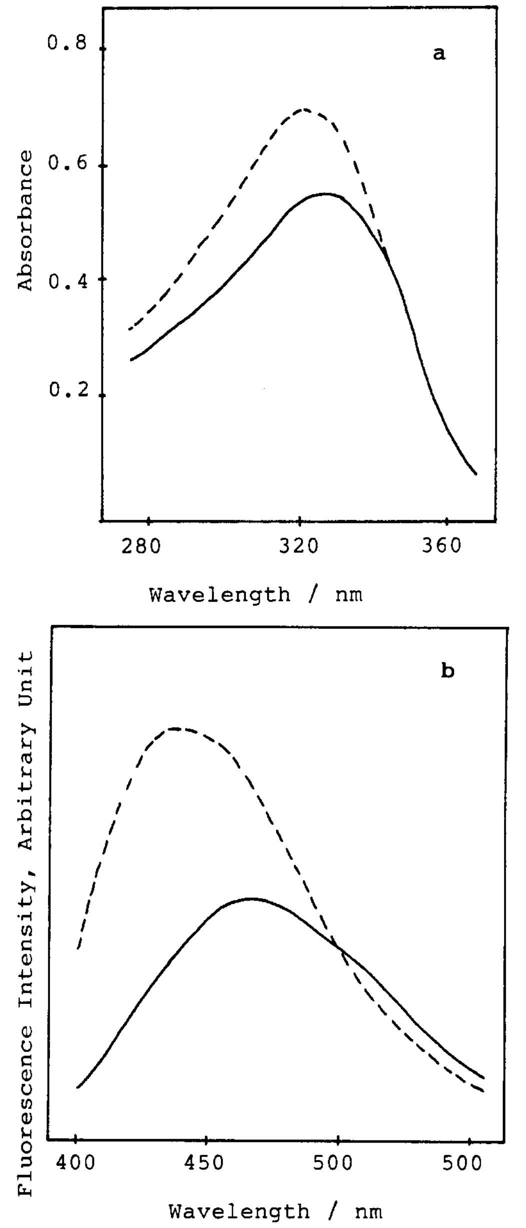

Figure 1. Absorption (a) and fluorescence (b) spectra of 4 and its KCl complex in MeOH at 25 °C (2.0×10^{-5} M, excitation 325 nm): —, 4; - - -, 4 + KCl (8.0×10^{-5} M).

Table II. Solvent Effects on Absorption and Fluorescence Properties of 4 at 25 °C (Excitation 365 nm)

	absorption		fluorescence	
solvt	λ_{max}, nm	ϵ_0	λ_{max}, nm	Φ_0
benzene	332	29 000	409	0.27
THF	330	46 000	436	0.27
CH_2Cl_2	329	45 000	437	0.28
MeOH	324	37 000	467	0.33
ZLI-2806[a]	340	50 000	412	*b*

[a] Eutecticmix liquid crystal (excitation 345 nm). [b] Not determined.

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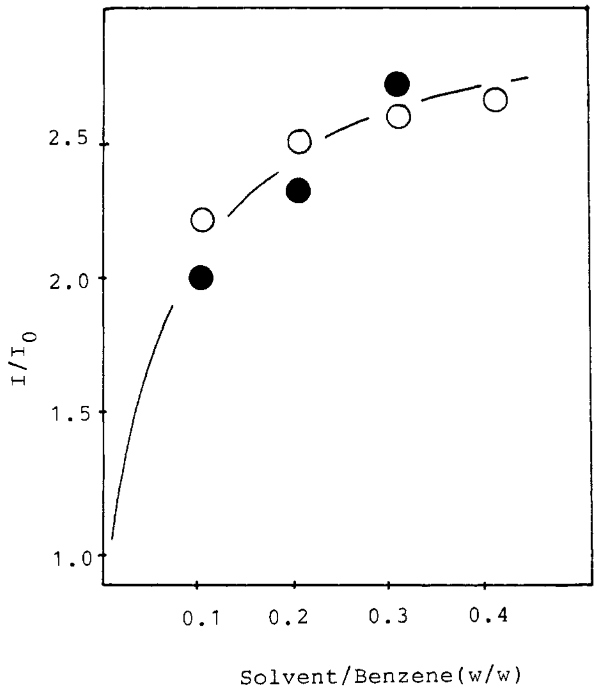
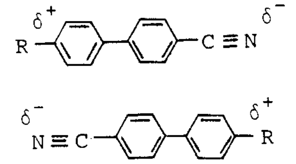


Figure 2. Influence of the composition of the mixing solvent (DMF–benzene and MeOH–benzene) on the fluorescence intensity of 4 at 25 °C (4.0×10^{-5} M); excitation 330 nm; emission 460 nm; ○, DMF–benzene; ●, MeOH–benzene.

Scheme II



maxima seen upon addition of polar solvents and reveals that DMF in benzene has a effect similar to that of MeOH in benzene on the fluoresence behavior. This result indicates that the solvent effect on the fluorescence stems from the polarity of the bulk solution and not from specific interactions between the crown ether ring and the solvent, such as hydrogen bonding. Usually, fluoroionophores show a bathochromic shift in both the absorption and fluorescence spectra in polar solvents since the excited state is generally more polar than the ground state. The bathochromic change in the fluorescence of 4 can be reasonably understood by the stabilization of the exited state (S′) in polar solvents, due to the presence of a donor group (crown ether ring) and an acceptor group (–CN) at the two ends of a long conjugated system. On the other hand, the unusual hypsochromic shift of the absorption maxima, i.e., the S state being less polar than the G state, may be explained as follows: For liquid crystals containing a cyano wing group, it is well-known that two molecules can form antiparallel correlations due to strong dipole–dipole interactions (Scheme II).[10] A similar interaction may also exist to some extent in the ground state of 4 in solutions. Because of the Franck–Condon effect, the interaction may be maintained in the first excited state (S)[9] and even become stronger than in the G state, since the polarized moiety might be excited to an ionic state. The resulting increase in the local interaction would lead to depression of the long-range charge separation between the two end groups (–O– in a crown ring and –CN), and the S state as a system may become less polar for solvents than the G state as shown in Scheme I. The dimer, however, would be expected to dissociate quickly to form the more stable and more polar monomeric form (S′ state) in the process. This explanation is in keeping with the fact that the difference in λ_{max} of fluorescence and absorption is very large and is also supported by the results of the following cation-induced effect.

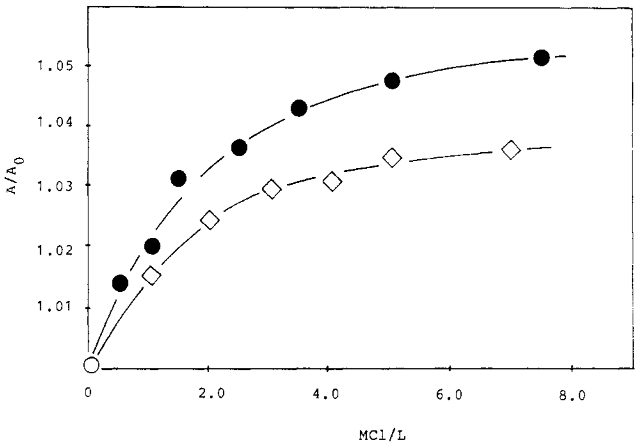


Figure 3. Influence of added alkali-metal cations on the optical density of the absorption maximum (325 nm) of 4 (8.0×10^{-6} M) at 25 °C in MeOH: ●, KCl; ◇, RbCl.

Table III. Stability Constants (K), Molar Excitation Coefficients (ϵ_c), and Quantum Yields (Φ_c) of Alkali-Metal Cation Complexes of 4 at 25 °C in MeOH

	absorption		fluorescence	
cation	log K	ϵ_c	log K	Φ_c
Na$^+$	*a*	*a*	4.32	0.58
K$^+$	4.80	52 000	4.91	0.58
Rb$^+$	4.36	43 000	4.31	0.50
Cs$^+$	*a*	*a*	3.88	0.42

[a] The changes in absorption maximum were too small to give accurate data.

The absorption and fluorescence spectra of 4 were affected by the addition of alkali-metal chlorides both in λ_{max} and in intensity (Figure 1). The spectral change can reasonably be attributed to the metal ion–crown ether interaction since no spectral change was observed for **2** and **3** at [MCl] < 10^{-3} M. Upon complexation a larger hypsochromic shift is observed in the fluorescence spectrum. Free 4 in methanol exhibits blue fluorescence, while in the presence of excess KCl the methanol solution of 4 is a violet color (λ_{max} from 465 to 435 nm). To this point, there have been many reports of crown ether compounds that show a color change in absorption upon cation binding, but examples of a color change associated with fluorescence are rather limited.[11] In the absorption spectrum only a small cation-induced hypsochromic shift, λ_{max} from 324 to 321 nm, was observed. Because in the S state the separated charge does not affect the oxygen of the crown ring, the destabilization of cation binding would be much smaller than in the S′ state.

Binding Constants (K) in Solution. In Figure 3, the increase in the absorbance of 4 (A/A_0 at 325 nm) upon

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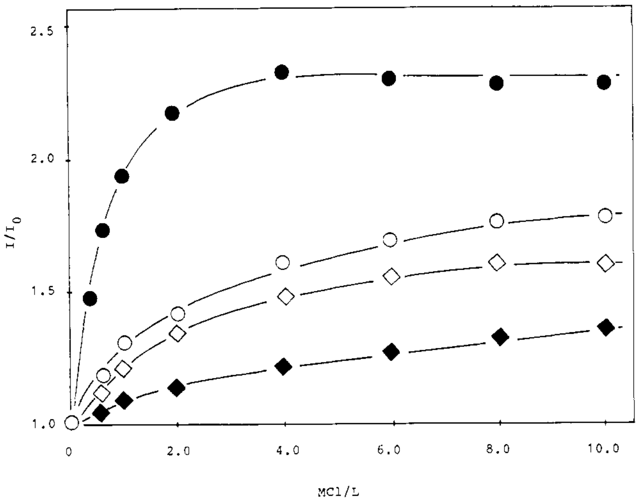

Figure 4. Influence of added alkali-metal cations on the fluorescence intensity of 4 (2.0×10^{-5} M) at 25 °C in MeOH (excitation 325 nm; emission 435 nm): ○, NaCl; ●, KCl; ◇, RbCl; ◆, CsCl.

addition of KCl and RbCl was plotted against cation concentrations. For the addition of NaCl and CsCl, however, the changes were too small to give accurate data ($A/A_0 < 1.02$). The binding constants (K) were estimated from the data on the basis of eq 1,[12,13] where ϵ_c is the molar

$$(1 - (A_0/A))/[\mathrm{M}^+] = (\epsilon_c/\epsilon_0)(A_0/A)K - K \qquad (1)$$

extinction coefficient of the complex. Plots of the values $(1 - (A_0/A))/[\mathrm{M}^+]$ vs A_0/A gave good straight lines with a correlation coefficient better than 0.98. K and ϵ_c, obtained from least-squares computation, are shown in Table III. Similarly, the cation-induced changes in fluorescence intensity were plotted in Figure 4 and treated by eq 2,[13]

$$(1 - (I_0/I))/[\mathrm{M}^+] = (\Phi_c/\Phi_0)(\epsilon_c/\epsilon_0)(I_0/I)K - K \qquad (2)$$

where Φ_0 and Φ_c are the quantum yields of fluorescence of 4 and its complex, and ϵ_0 and ϵ_c are the molar extinction coefficients of 4 and the complex at the wavelength of the exciting light, respectively. The ϵ_c/ϵ_0 values at 325 nm are 1.12, 1.41, 1.16, and 1.29 for Na^+, K^+, Rb^+, and Cs^+, respectively. The results are summarized in Table III. An examination of Table III reveals the following facts. The K values estimated from both absorption and fluorescence data are very close and are approximately comparable to or somewhat smaller than those reported for benzo-18-crown-6 and its homologues, except for the data of the Na^+ complex from the fluorescence experiment.[14] The affinity of 4 for alkali-metal cations decreases in the order $\mathrm{K}^+ > \mathrm{Na}^+ > \mathrm{Rb}^+ > \mathrm{Cs}^+$. The unusually large K value for the Na^+ complex may arise from the photometric nature of the measurements used in this study. The evaluation of K values by conventional methods is based on the changes in metal cation activity in solutions. In this study, the changes in spectra from which K values were calculated were based on the interaction of the phenolic oxygen atoms in the benzo crown unit with cations. The small cation Na^+, with high charge density, can situate itself more deeply into the macroring and is expected to exert a much stronger effect on the entire conjugated system than the other cations, which may result in an increase when evaluating the K value. A similar reasoning, based on the proximity of a cation to the crown ring, may be advanced to explain the fact that no spectral change was observed for 3 on addition of Na^+ or K^+, together with the lower binding ability of the benzo-15-crown-5 unit. The complexes of 4 exhibit larger quantum yields of fluorescence than free 4, i.e., $\Phi_c > \Phi_0$, although some heavy-atom effects can be found in the complexes of Rb^+ and Cs^+, which is consistent with the results of fluorescence studies of other crown ether compounds reported previously.[12,15,16]

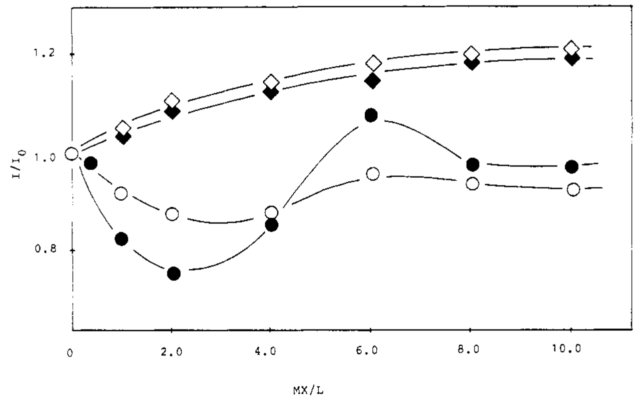

Figure 5. Influence of added alkali-metal salts on the fluorescence intensity of 4 (2.0×10^{-5} M) at 25 °C in THF (excitation 345 nm; emission 430 nm): ○, NaSCN; ●, KSCN; ◇, $\mathrm{NaClO_4}$; ◆, $\mathrm{KClO_4}$.

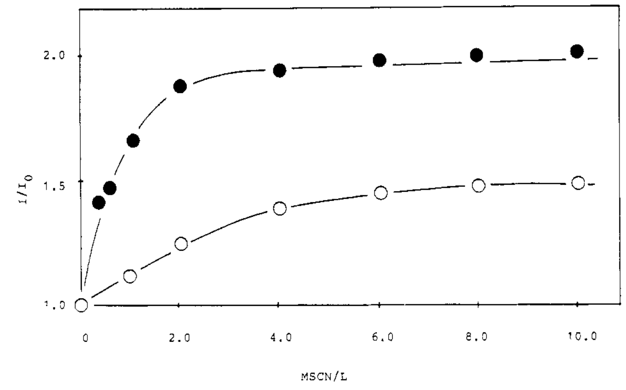

Figure 6. Influence of added MSCN on the fluorescence intensity of 4 (2.0×10^{-5} M) at 25 °C in MeOH (excitation 335 nm; emission 440 nm): ○, NaSCN; ●, KSCN.

Quenching Effect of Thiocyanate Anion. Figures 5 and 6 show the cation-induced effect on fluorescence for the systems MSCN–4 in THF, $\mathrm{MClO_4}$–4 in THF, and MSCN–4 in MeOH, respectively (M = Na, K). Strangely, the plots of I/I_0 against cation concentrations for MSCN–4 in THF showed a biphasic dependence, indicating that besides the enhancement from the cation binding there is another effect that reduces the fluorescence. Since a similar phenomenon was not observed for $\mathrm{MClO_4}$ under the same conditions, the unusual observation for MSCN can be explained by the quenching effect of the SCN^- anion. In fact, fluorescence quenching titrations with SCN^- have been previously used by Vögtle et al. to determine the binding constants of crown ethers and other ligands in solution.[4,17] In the less polar solvent THF the com-

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Table IV. Stability Constants (K) and Quantum Yields (Φ_c) of Alkali-Metal Cation Complexes of 4 at 25 °C from Fluorescence Data

salt-solvent	log K	Φ_c^b
$NaClO_4$-THF	3.96	0.32
$KClO_4$-THF[a]	4.08	0.24
NaSCN-MeOH	4.04	0.52
KSCN-MeOH	4.88	0.49

[a] The accuracy of the data is somewhat inferior since $KClO_4$ does not dissolve completely in THF. [b] The ϵ_c/ϵ_0 values from MCl-MeOH systems were used in the calculation; see text.

plexed cation and the counteranion are expected to form a contact ion pair through which the fluorescence of the ligand can be quenched efficiently. In the polar solvent MeOH, however, a separated ion pair between the cation and counteranion makes the quenching effect negligible, as shown in Figure 6. For the systems that are free from this quenching effect the binding constants were calculated by the method described above and are summarized in Table IV. The accuracy of the data for $KClO_4$-4 in THF is somewhat inferior because the salt could not be dissolved completely in THF under the conditions used. For MSCN-MeOH systems the stability constants (K) are very close to those from MCl-MeOH systems, indicating that the counteranion does not influence the complexation of 4 in MeOH. Furthermore, in both KCl-4 and KSCN-4 systems a break in the fluorescence intensity was observed near the equimolar ratio in Figures 4 and 6, respectively, which suggests a 1:1 stoichiometry for these complexes; a similar break in the I/I_0-M/L profile for the other cation complexes is not as clear, probably because of their low binding abilities.

Complexation Behavior in the Nematic Phase. As shown in Table II the solvent effect of ZLI-2806 on the fluoroionophore 4 is similar to that of benzene. In the mesophase of the liquid-crystalline compounds, heightened interactions between the fluoroionophores (3 or 4) and the solvent molecules can be expected, along with the dimeric association mentioned above. Both the enhancement of the intermolecular interactions and the lesser polarity of the solvent would result in a reduction of the contribution from the highly charge-separated structure. The solution can be treated as a eutectic nematic solution, and the orientation of the molecules is the same, with the solvent being oriented parallel to the cell plane. Thus, there is no need to consider the influence of molecular orientation on the fluorescent behavior.[18]

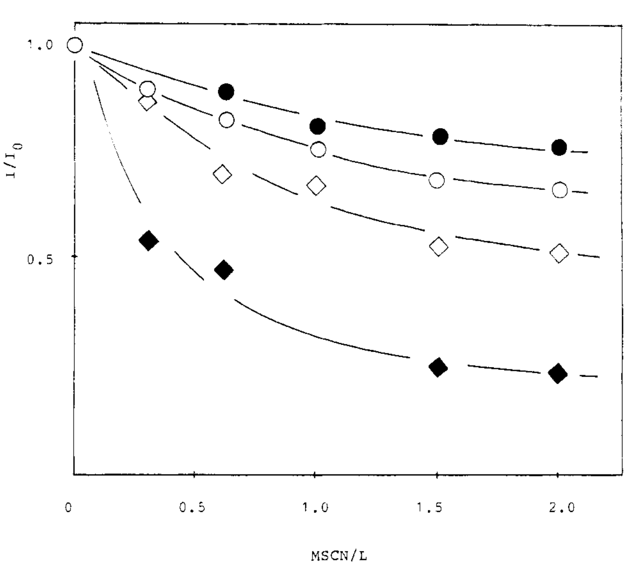

Figure 7. Influence of added MSCN on the fluorescence intensity of 3 and 4 (1.3×10^{-3} M) at 25 °C in ZLI-2806 (excitation 345 nm; emission 410 nm): ○, 3-NaSCN; ●, 3-KSCN; ◇, 4-NaSCN; ◆, 4-KSCN.

Table V. Stability Constants (K) of MSCN complexes of 3 and 4 at 25 °C in ZLI-2806

	log K	
ligand	NaSCN	KSCN
3	3.2 ± 0.1	2.5 ± 0.2
4	3.7 ± 0.1	4.3 ± 0.1

As expected, the addition of alkali metal chloride did not have any appreciable effect on the absorption and fluorescence spectra of 3 or 4 in the nematic solvent. On addition of MSCN (M = Na, K), the intensities of the fluorescence of 3 and 4 in ZLI-2806 decreased, but the spectral patterns were unchanged. Since analogous intensity changes were not found for "non-crowned" compounds 1 and 2, the decrease associated with 3 and 4 can be considered to arise from the cation-crown interaction due to the quenching of SCN^- through a contact ion pair. The decreases in intensity of the fluorescence maximum at 410 nm were plotted against cation concentration and are shown in Figure 7. In the liquid-crystalline state, quenching by SCN^- may be considered a static quenching, i.e., only within one molecular complex can fluorescence on the ligand be quenched by the counteranion. On this basis, binding constants K can be calculated by using eq 3 and 4. Equation 3 is an equation that pertains to

$$I/I_0 = 1 + T(I_c - I_0)/I_0 \qquad (3)$$

fluorescence measurements, where I_0 and I_c are the fluorescence intensities of the free ligand and its cation complex, respectively.[17] In the case of a 1:1 binding equilibrium, T can be defined as

$$T = \tfrac{1}{2}(1 + 1/K[\mathrm{L}]_0 + [\mathrm{M}^+]_0/[\mathrm{L}]_0) \times \left[1 - \left(1 - \frac{4[\mathrm{M}^+]_0/[\mathrm{L}]_0}{(1 + 1/K[\mathrm{L}]_0 + [\mathrm{M}^+]_0/[\mathrm{L}]_0)^2}\right)^{1/2}\right] \qquad (4)$$

The binding constants K were evaluated by using a nonlinear least-squares analysis, starting from approximate values for K and I_c. The best fit data obtained by systematic variation of the two parameters and the average values of K evaluated from two independent measurements are shown in Table V, along with their standard deviations. As can be seen from Table V, selective complexation of crown ethers with alkali-metal cations does exist in the nematic liquid-crystalline state, although the differences in affinity among these complexes are relatively small. The stability of the complexes decreases in the order 4-(B18C6)-K^+ > 4(B18C6)-Na^+ > 3(B15C5)-Na^+ > 3-(B15C5)-K^+. In methanol, however, it was reported that the order is 18C6-K^+ > 18C6-Na^+ > 15C5-K^+ > 15C5-Na^+.[14] For benzo crown ethers in 90% (w/w) aqueous methanol solution the affinity is also in the order B18C6-K^+ > B18C6-Na^+ > B15C5-K^+ > B15C5-Na^+.[14] Generally, K values determined in less polar solvents will be higher than those determined in more polar solvents.[19] Since ZLI-2806 can be considered a nonpolar solvent, the complexation in ZLI-2806 should be much stronger than in other, more polar solvents. However, the binding con-

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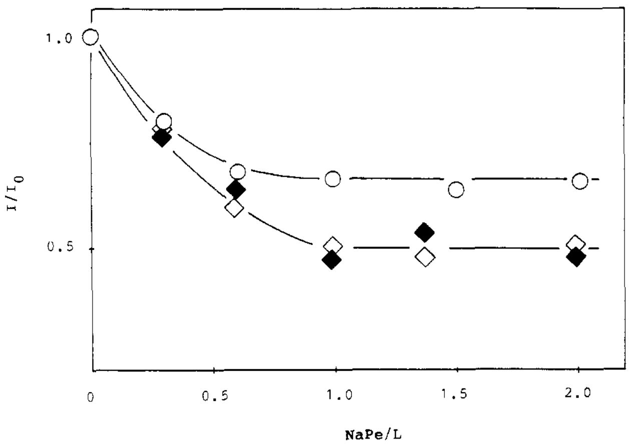
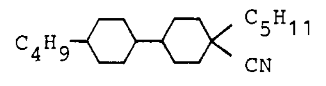


Figure 8. Influence of added NaPe on the fluorescence intensity of **2** (○), **3** (◇), and **4** (◆), 1.3×10^{-3} M at 25 °C in ZLI-2806 (excitation 345 nm; emission 410 nm).

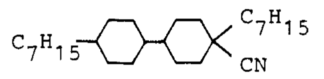
stants K here are approximately comparable to or somewhat smaller than those in methanol.[14] In methanol the large binding constants for 15-crown-5 and benzo-15-crown-5 with K^+ ion have been explained by the formation of a 2:1 crown unit:cation complex,[14b] but no evidence for such a 2:1 stoichiometry in the complexation of **3** with KSCN was obtained either in methanol or in ZLI-2806 here. Combined with the results described before[6] it is clear that the hole size:cation diameter relationship also holds in the nematic state, but the factors affecting the complexation may be considerably different from those observed in common solvents.

Perylene derivatives have been widely used as fluorescent probes to study fluorescence and energy transfer behavior in solvents and liquid crystals, due to their unique absorption and fluorescence properties.[18,20] In this study an attempt was made using sodium 3-perylenecarboxylate (NaPe) to investigate the effect of cation–crown ether complexation on energy transfer between the ligands and the counteranion in the nematic phase. Energy transfer was indeed observed for the fluoroionophore (**3** or **4**)–NaPe systems, as evidenced by a decrease in the ligand fluorescence (410 nm) and an increase in the counteranion fluorescence (480 nm) upon addition of NaPe under excitation at 345 nm, where NaPe has no absorption. As shown in Figure 8, however, the "non-crowned" compound **2** gave a similar result, and the quenching effect of NaPe for **3** and **4** was the same, i.e., quenching occurs regardless of whether the crown–cation interaction exists or not. In the case of SCN^- described above, the quenching may be due to an electron-transfer-like mechanism due to the low oxidation potential of the quencher. Generally, such quenching occurs over a short distance, ca. 10 Å,[21] so the SCN^- anion could affect the fluorescence of the ligand within the complex only through a contact ion-pair interaction. With perylene derivatives, however, quenching occurs through an energy-transfer mechanism, which may extend over a relatively long distance, ca. 50 Å or more.[22] As can be seen in Figure 8, the fluorescence decreases with increasing [NaPe] in the range of [NaPe]/[ligand] < 1 but is nearly unaffected by further increases in [NaPe]. The results indicate that every molecule of the quencher NaPe in the system, both complexed and uncomplexed, can quench the fluorescence of the ligands, and no effect from the cation–crown interaction on the quenching was observed under the present conditions.

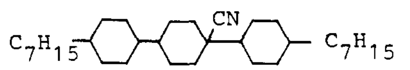
Chart II. Main Composition and Properties of the Eutectic Mix Liquid Crystal ZLI-2806



4-cyano-4-heptyl-4'-butyl-1,1'-bicyclohexane, 20%



4-cyano-4-pentyl-4'-pentyl-1,1'-bicyclohexane, 21%



1,4-bis(4-pentyl-1-cyclohexyl) 1-cyclohexanecarbonitrile, 22%

$$\mathrm{K} \overset{-30\,°\mathrm{C}}{\rightleftharpoons} \mathrm{N} \overset{100\,°\mathrm{C}}{\rightleftharpoons} \mathrm{I}$$

$\nu = 57\ \mathrm{mm}^2\ \mathrm{s}^{-1}$ at 20 °C

$\Delta\varepsilon = -4.8$

Conclusion

The "crowned" liquid-crystalline compounds, 4'-((p'-cyanobiphenylyl)ethynyl)benzo crown ethers, showed both a solvent effect and a cation-induced effect, both in absorption and in fluorescence, which can be explained by a mechanism incorporating a dimerization of the crown ethers in the excited state. The cation-induced spectroscopic changes were used in evaluating the cation-binding abilities of the crown ethers in polar solvents and yielded results similar to those obtained from other methods. The fluorescence quenching method with thiocyanate was successfully applied to the complexation in the eutectic nematic solution (ZLI-2806), and the results revealed that crown ether compounds also interact with alkali-metal cations selectively in the nematic phase and that the binding ability in the eutectic nematic solution is comparable with that seen in methanol solution. There is no evidence, however, for 2:1 (crown unit:cation) complexation of 4'-((p'-cyanobiphenylyl)ethynyl)benzo-15-crown-5 with KSCN in the nematic phase. Furthermore, the energy-transfer quenching in NaPe/**3** and NaPe/**4** systems did not show any specific cation–crown ether interaction under the same conditions.

Experimental Section

General Procedures. All solvents were distilled before use. Alkali-metal salts were of analytical grade and were used without further purification except for drying. Preparation of the liquid-crystalline compounds bearing crown ether rings was described

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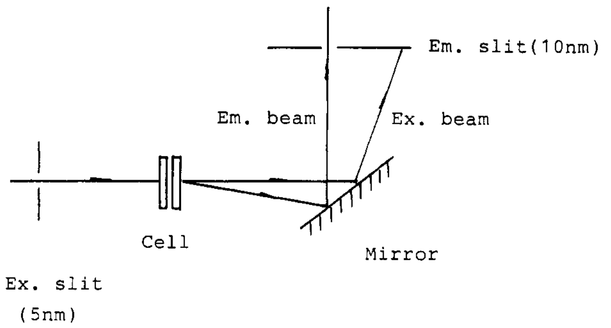

Figure 9. System arrangements for fluorescence measuring of liquid-crystal cell.

in previous papers,[6] and their structures and transition temperatures are given in Chart I. The nematic liquid crystal ZLI-2806, used here as a solvent, was available from E. Merck Co., which is a eutectic mix of cyanocyclohexyl type liquid crystals, as shown in Chart II. ZLI-2806 is a transparent, relatively low-viscosity liquid crystal and has no absorption in the region above 250 nm.

Sodium 3-Perylenecarboxylate (NaPe). Sodium 3-perylenecarboxylate was prepared as follows. Perylenecarboxylic acids (4 g), a mixture of carboxy-substituted derivatives from Mitsui Toatsu Chemicals, Inc., were refluxed in 30 mL of butyl bromide and 20 mL of triethylamine for 10 h. After cooling and concentration, the residue was extracted with chloroform, and the organic phase was dried over $MgSO_4$. The solvent was removed by evaporation, and recrystallization of the crude product from benzene gave dibutyl 3,9-perylenedicarboxylate (DBPe) as orange plates. The residue from the filtrate was then treated by chromatography (silica gel/benzene). The first green-yellow band gave a small amount of perylene, and from the second yellow band 0.2 g of butyl 3-perylenecarboxylate (BPe) was obtained, which was further purified by recrystallization from heptane. The third large orange band was the mixture of dibutyl perylenedicarboxylates. Hydrolysis of BPe by NaOH in EtOH at reflux for 5 h gave NaPe as golden crystals (from EtOH:H_2O 10:1).

DBPe: orange crystals; mp 205–207 °C; IR (Nujol) 1700, 1250, 1180, 1120, 810, 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.5–2.5 (m, 14 H), 4.2–4.6 (t, 4 H), 7.1–8.0 (m, 8 H), 8.6–8.8 (d, 2 H).

BPe: yellow crystals; mp 154–157 °C; IR (Nujol) 1700, 1250, 1180, 1120 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.8–2.0 (m, 7 H), 4.2–4.5 (t, 2 H), 7.1–8.1 (m, 10 H), 8.6–8.8 (d, 1 H); MS, *m/e* 352 (M^+).

NaPe: golden crystals, mp > 300 °C; IR (Nujol) 3400, 1580, 1500, 820, 770 cm^{-1}; UV [λ_{max}, nm (ϵ)] in MeOH 441 (33 000), 415 (26 000), 255 (28 000), in ZLI-2806 458 (25 000), 434 (24 000), 259 (30 000); fluorescence (λ_{em}, nm) in MeOH (λ_{ex} 415 nm) 478, 455, in ZLI-2806 (λ_{ex} 435 nm) 500, 470. Anal. Calcd for $C_{21}H_{15}O_4Na$ (NaPe + $2H_2O$): C, 71.18; H, 4.27. Found: C, 70.96; H, 4.32.

Measurement. Absorption and emission spectra in solutions were measured with a Shimadzu UV-200 spectrophotometer and Shimadzu RF-500 spectrofluorometer, respectively, in a 10 × 10 mm quartz cell. The emission measurement was conducted under aerated conditions, since no spectral change was observed under air-saturated vs Ar-saturated conditions. Quantum yields of fluorescence in solutions were determined by comparison with that of a quinine bisulfate–0.1 N H_2SO_4 solution ($\Phi_f = 0.55$).[23]

Measurements for liquid-crystalline samples are as follows. The samples were prepared by dissolving ZLI-2806 in dichloromethane solutions of the fluoroionophore, and then varied amounts of MSCN in methanol were added. The solvent was removed by gentle heating, and the resulting samples were melted to an isotropic phase by heating above 100 °C. After cooling, the samples thus obtained were kept under reduced pressure for over 48 h at room temperature. A cell for holding the liquid-crystalline samples was constructed with two quartz plates and plastic spacers (10 μm). Molecular alignment of the samples was defined by rubbing the plates' surfaces so that the axes of the liquid-crystalline molecules would lie along the rubbing direction. Absorption measurements were carried out with a Shimadsu UV-160 spectrophotometer. The λ_{max} and ϵ_0 of 4 in ZLI-2806 are given in Table II. Fluorescence spectra were measured with a Shimadsu RF 500 fluorospectrometer. The cell was held on a temperature-controlled aluminum block (25 °C) and irradiated with an incident light beam perpendicular to the cell plane. The transmitted light was reflected by an aluminum-coated mirror to the perpendicular, where the detector system was located (Figure 9).[18]

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