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SYNTHETIC MACROCYCLIC LIGANDS. VI.[1] LITHIUM ION-SELECTIVE FLUORESCENT EMISSION WITH CROWNED BENZO- AND NAPHTHO-THIAZOLYLPHENOLS

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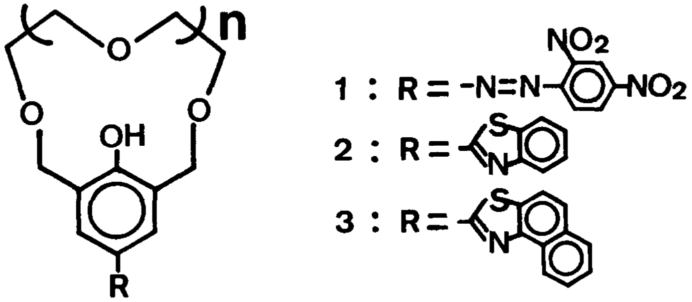
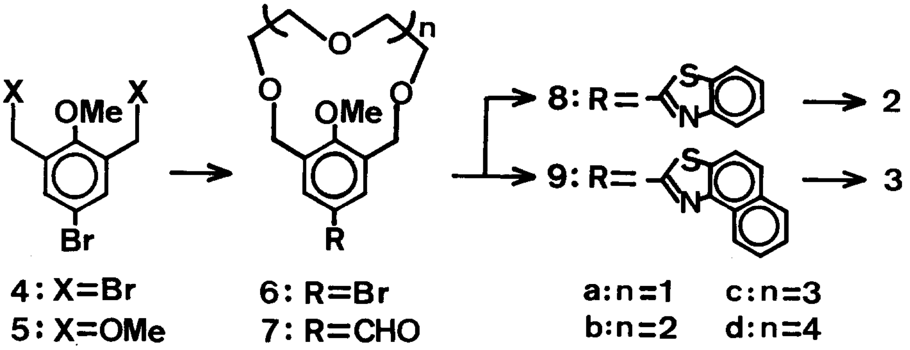
Abstract: Synthesis of fluorescent crowned benzo- and naphtho-thiazolylphenols are described and lithium ion-selective fluorescent emission is observed under the restricted conditions.

In previous papers concerning applications of host-guest complexation, we reported the syntheses of some host molecules modified with appropriate chromophores by such a way that the complexation was accompanied by significant changes in color[2)] and fluorescence[3)]. Crowned dinitrophenylazophenol **1**[2d)] and related systems[2e)] have been provided as a typical example of such remarkable color change, and **1b** has been applied to the spectrophotometric determination of alkali metal ions.[4)] Considering that benzothiazolylphenols fluoresce strongly in alkaline solution,[5)] new fluorescent cyclic polyethers **2** and **3** were designed and expected to be superior to the azo dye **1** in sensitivity toward metal ions. This paper deals with the synthesis of **2** and **3** and their ion-selective fluorescent emission.

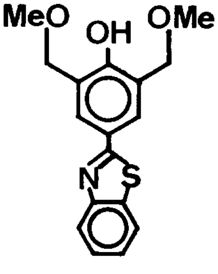


a: n=1
b: n=2
c: n=3
d: n=4

Cyclic polyether intermediates **6**[6)] were prepared by cyclization of the corresponding oligoethylene glycol with **4**[6)] derived from 4-bromo-2,6-bis(hydroxymethyl)phenol[7)] and were converted to **7**[6)] with butyllithium and DMF in 74-90% yield. Reaction of **7** and o-aminothiophenol or 2,2'-dithiobis(1-aminonaphthalene)[8)] gave benzo- or naphtho-thiazolyl derivative **8**[6)] or **9**[6)] in 49-80% yield.



Demethylation of **8** and **9**, which was the key step of the present synthesis, was carried out by treatment with sodium ethanethiolate[9)] in DMF to yield the desired phenols **2**[6)] and **3**[6)], respectively, in excellent yields. Similarly, non-crowned benzothiazolylphenol **10**[6)] was prepared via **5**[6)] for reference.



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Although neither **2** nor **10** in chloroform[10)] dissociates even in the presence of excess triethylamine, addition of crystalline metal salts immediately gives rise to remarkable changes in absorption spectra, indicating the formation of the phenolate anion (Figs 1 and 2). On irradiation of the heterogeneous specimen containing the predominant phenolate, strong blue-violet fluorescence of the solution was observed.[12)] The results of screening for the fluorescent emission

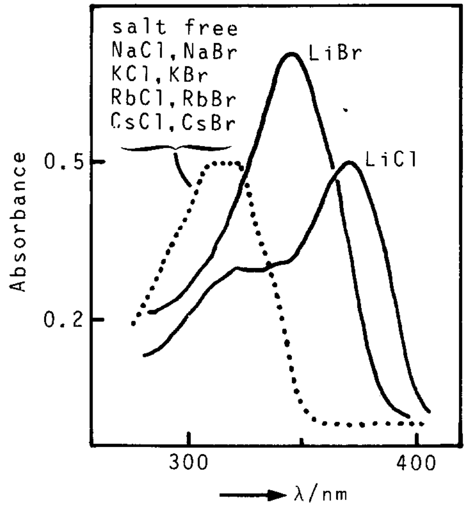

Fig. 1. Absorption spectra of **2b**-alkali metal halide-Et_3N systems in $CHCl_3$.[11)]

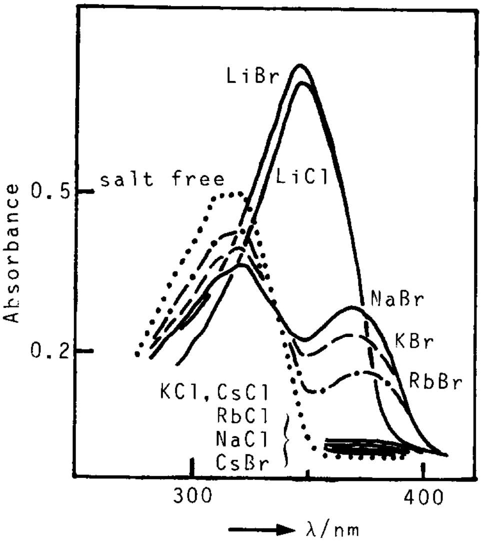

Fig. 2. Absorption spectra of **2c**-alkali metal halide-Et_3N systems in $CHCl_3$.[11)]

Table. Salt-induced fluorescence a) for dye-salt-Et_3N systems in $CHCl_3$. 11)

Salt\Dye		**2a**	**2b**	**2c**	**2d**	**10**
Li	Cl	+++(365) b)	+++(371)	+++(347)	+++(351)	– c)
	Br	+++(347)	+++(347)	+++(347)	+++(347)	+++(345)
	ClO_4	+++(364)	+++(348)	+++(345)	+++(348)	+++(339)
MX d)		–	–	+(367-372) e)	+(368-373) f)	–

a) "+++" and "+": strong and weak, respectively. b) Numbers in parentheses show the wavelengths of absorption maxima in nm. c) No appreciable change in fluorescence and absorption spectra. d) M=Na, K, Rb, and Cs; X=Cl, Br, and ClO_4. e) K-, Rb-, and $KClO_4$ are inactive. f) NaCl, KCl, $KClO_4$, and $RbClO_4$ are inactive.

are summarized in Table. The dyes with smaller ring size, **2a** and **2b**, show lithium ion-selective emission among the alkali metal salts, while ones with larger cavity, **2c** and **2d**, tend to bind larger alkali metal ions as well as for lithium ion. The lithium ion-selective fluorescent emission should be attributed to the two cooperative factors, i.e., the acid dissociation accelerated by interaction of the dye with the salt and the electrostatic binding of the cation with the resulting fluorescent anion, and may provide a qualitative way to detect a small amount of lithium from bulk of the other alkali metal ions.

The fact that acyclic dye **10** without cavity is still active toward lithium bromide and perchlorate would be responsible for the existence of two extra ether oxygens located near the hydroxyl group. Noteworthy is the different behavior of **2** and **10** toward lithium chloride. The dyes **2c** and **2d** interact with this salt to form the phenolate completely, whereas **10** is inactive; **2a** and **2b** with smaller cavity lie between the two extremes. This finding demonstrates that the cavity of the present dyes plays an important role in increasing their sensitivity on the complexation. Unexpected red-shifts observed for **2a**-LiCl and -$LiClO_4$ and **2b**-LiCl systems seem to suggest the formation of an intricate aggregate composed of the dye, metal salt, and base.

References and Notes

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6) All new compounds showed satisfactory elemental analyses and spectral properties with the exception of the analyses of **2d**, **5**, and **7a**. **2a:** colorless prisms (MeOH), mp 149-150 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 8.07-7.90 (s, 2H, ArH), 7.85 (s, 2H, ArH), 7.73 (s, 1H, OH), 7.56-7.26 (s, 2H, ArH), 5.27 (d, J=13.2 Hz, 2H, ArCH$_2$), 4.36 (d, J=13.2 Hz, 2H, ArCH$_2$). **2b:** colorless thin plates (ethyl acetate), mp 155-156 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 8.17 (s, 1H, OH), 8.06-7.83 (m, 2H, ArH), 7.85 (s, 2H, ArH), 7.48-7.33 (m, 2H, ArH), 4.73 (s, 4H, ArCH$_2$). **2c:** pale yellow thin plates (MeOH), mp 132.5-133.5 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 8.49 (s, 1H, OH), 8.05-7.82 (m, 2H, ArH), 7.88 (s, 2H, ArH), 7.53-7.32 (m, 2H, ArH), 4.77 (s, 4H, ArCH$_2$). **2d:** colorless oil; ^{1}H NMR (100 MHz, CDCl$_3$) δ 8.44 (bs, 1H, OH), 8.06-7.82 (m, 2H, ArH), 7.90 (s, 2H, ArH), 7.53-7.26 (m, 2H, ArH), 4.79 (s, 4H, ArCH$_2$), 3.83-3.52 (m, 20H, OCH$_2$CH$_2$O). **3a:** pale yellow crystals (benzene-hexane), mp 194-196 °C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 7.95 (s, 2H, ArH), 5.30 (d, J=8.7 Hz, 2H, ArCH$_2$), 4.40 (d, J=8.7 Hz, 2H, ArCH$_2$). **3b:** colorless foam, mp 142.5-143°C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 8.12 (bs, 1H, OH), 7.95 (s, 2H, ArH), 4.77 (s, 4H, ArCH$_2$). **3c:** pale yellow plates (ethyl acetate), mp 136.5-137.5 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 7.98 (s, 2H, ArH), 4.80 (s, 4H, ArCH$_2$). **3d:** pale brown plates (CH$_3$CN), mp 105-106 °C; ^{1}H NMR (360 MHz, CDCl$_3$) δ 8.36 (bs, 1H, OH), 8.00 (s, 2H, ArH), 4.83 (s, 4H, ArCH$_2$). **10:** colorless needles (hexane), mp 72-73 °C; ^{1}H NMR (100 MHz, CDCl$_3$) δ 8.29 (s, 1H, OH), 7.89 (s, 2H, ArH), 4.69 (s, 4H, ArCH$_2$), 3.50 (s, 6H, OMe).

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10) Since a fairly good lithium ion-selective coloration with the azo dye has been effected in chloroform,$^{1)}$ the same medium was used in this work.

11) The electronic spectra were measured as follows. After a spoonful of crystalline salt (ca. 10^{-4} mol) was added to a stock solution (ca. 10^{-5} M, 3.5 ml) of the dye containing triethylamine (ca. 10^{-6} mol) in a cell, the resulting mixture was well shaken for 1 min and then the spectra were recorded and the fluorescence emitted on irradiation with a hand-held UV lampwas qualitatively checked by visual manner.

12) Unfortunately, reliable fluorescence spectra could not be determined under the given conditions because of both unstability of the fluorescence and the heterogeneous system. However, 0.5% methanol-benzene used as the solvent for the determination of lithium ion gave reproducible excitation and emission spectra with maxima at 375 and 410 nm, respectively.$^{3b)}$

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