

# Cation Selective Complexation-Coloration with Chromophoric Crowns

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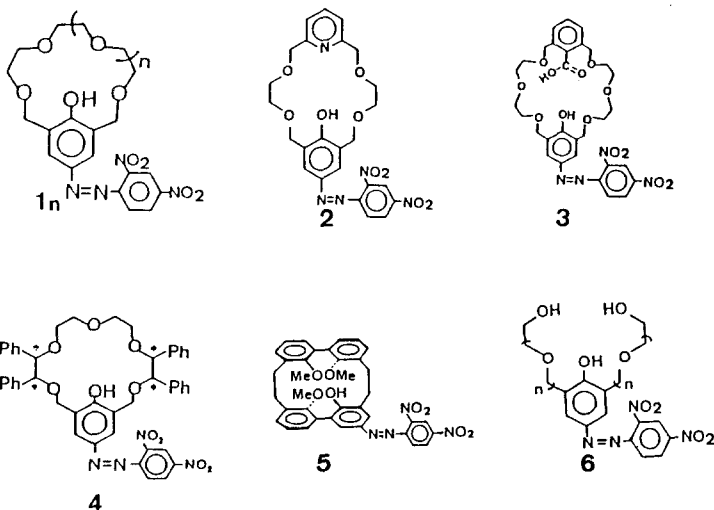
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**Abstract.** Amine selective complexation-coloration of some azophenol-dyed crowns and X-ray structures of two secondary amine complexes are reported as well as lithium ion specific coloration with an azophenol spherand.

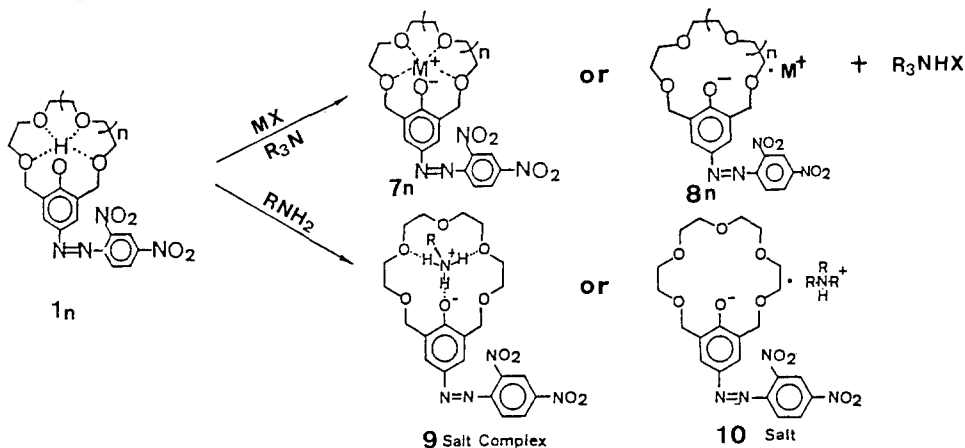
**Key words.** Azophenol crown ether, cation, lithium.

## 1. Introduction

The design and synthesis of a series of ligands which can selectively bind a given metal or organic ion and undergo concurrently a color change are subjects in host-guest chemistry which have been highlighted recently [1]. Previously we reported lithium ion selective coloration with azophenol-dyed crowns [2], fluorescent emission with benzothiazolylphenol crowns [3], and their application to lithium ion analysis. We attempted the structural recognition of protonated amines by the use of azophenol crowns 1–4, spherand 5, and podand 6, which have a phenolate anion in the center. The colored complexes, 7 and 9, of these crowns with metal or ammonium ion are differentiated from simple ion-dipole type complexes by an additional binding force, that is, coulombic interaction between phenolate anion and the guest cation. Now we report amine-selective and enantiomer-selective complexation-coloration

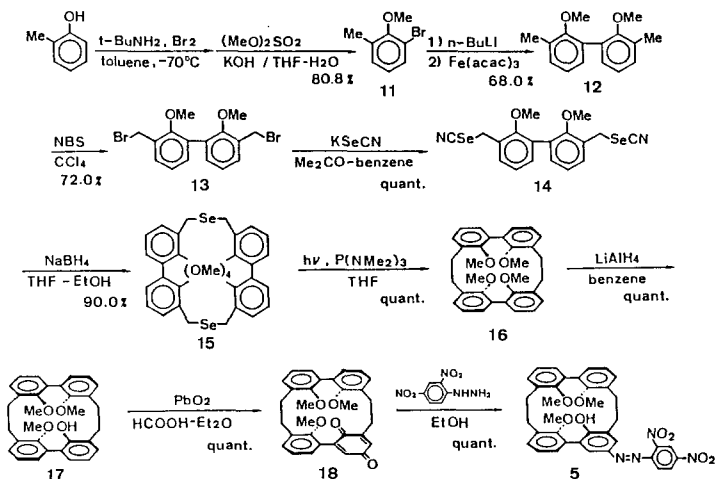


with azophenol crowns as well as lithium ion specific coloration with a spherand analog.



## 2. Discussion

(2.1) With the intention of achieving much higher selectivity for lithium ion complexation, a spherand type host **5** containing a dinitrophenylazophenol moiety was designed and synthesized by the use of a key step, photodeselenation which developed previously (Scheme 1) [5].



Scheme 1.

In chloroform, no phenolate anion of **5** was detected even in the presence of excess piperidine as a base. When crystalline lithium salts were added to this solution, a dramatic color change from yellow to violet took place rapidly, except for nitrate, fluoride, and sulfate. This phenomenon indicates evidently the formation of the lithium phenolate. On the other hand, no tendency of the interaction was observed with any of the other 58 metal salts listed in Fig. 1.

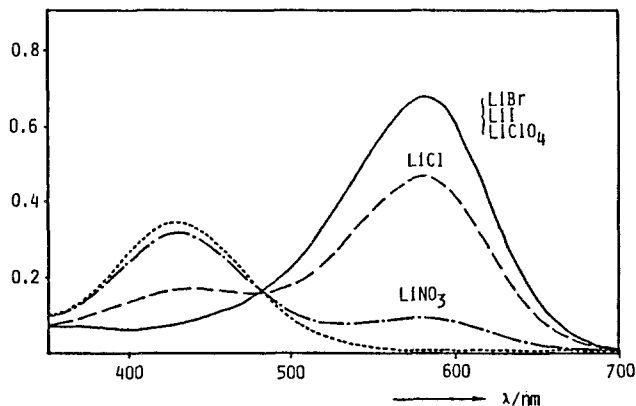


Fig. 1. Visible spectra of spherand-salt-piperidine systems in  $\text{CHCl}_3$ . - - - : Salt-free,  $\text{LiF}$ ,  $\text{Li}_2\text{SO}_4$ ,  $\text{BeCl}_2$ ,  $\text{MX}$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{NO}_3, \text{SO}_4$ ),  $\text{MX}_2$  ( $\text{M} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{ClO}_4$ ),  $\text{MX}_2$  ( $\text{M} = \text{Mn}, \text{Co}, \text{Ni}, \text{Zn}, \text{Cd}, \text{Sn}, \text{Hg}$ ;  $\text{X} = \text{Cl}$  or  $\text{Br}$ ),  $\text{MCl}_3$  ( $\text{M} = \text{Al}, \text{Cr}, \text{Fe}, \text{Sb}, \text{Ce}, \text{Bi}$ ),  $\text{Pb}(\text{OAc})_2$ ,  $\text{AgClO}_4$ .

In the hydrophobic solvent, the lithium ion of the colored species must be accommodated in the hydrophilic cavity of the host anion on the basis of the following facts: (i) the cavity is expected to be small but able to accommodate the guest, (ii) the coloration takes place only when the specimen is in contact with Li salts, (iii) the monodemethylation of spherand **16** to **17** occurs exclusively in aprotic solvent such as benzene even in the presence of excess  $\text{LiAlH}_4$ , (iv) no cation exchange between  $\text{Li}^+$  and  $\text{Ca}^{2+}$  or  $\text{Ba}^{2+}$  was observed.

The observed perfect lithium selectivity under the given conditions is described in terms of binding the guest ion by coulombic attraction and ion-dipole interactions and rejecting larger or multivalent cations by the steric effect caused by the narrow entrances to the small cavity in the spherand **5**.

(2.2) Another type of complexation with crown ethers is concerned with a tripod arrangement by three ether oxygens of the crown ether. We recently observed such a perching type complexation of protonated amines by the use of the above-stated azophenol crowns.

The azophenol crown **1** does not dissociate in chloroform, but shows the formation of the phenolate-ammonium complex in the presence of amines in their absorption spectra. Thus the formation of the salt complex **9** with amine is strongly dependent upon the structure of the amines but not their basicity. For example, absorption maxima of **1** ( $n = 1-3$ )-amine complexes appear in the shorter wavelength region compared to those of acyclic reference azophenols like **A** and **B** in Figure 2. The figure also shows that acyclic hosts reveal nearly constant values of the maxima regardless of the amine species. The complexes of dimethylamine show, in general, blue shifts of their maxima in any solvent. On the other hand, **1<sub>1</sub>** shows larger absorbances of the salt complexes with relatively less bulky amines compared to those of bulky amines. The **1<sub>1</sub>**-piperidine (1:1) complex was purified and determined by X-ray analysis to be a typical perching type structure where the whole chromophore is coplanar and nearly perpendicular to the crown ring (Figure 3) [5].

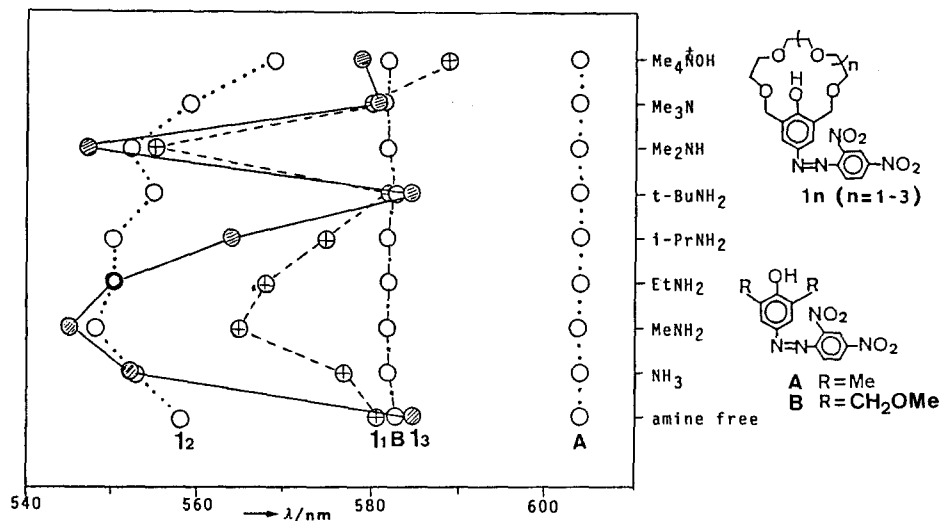


Fig. 2. Absorption maxima of azophenol dye-amine systems in EtOH.

Next, the complexation of azophenol crown **3** containing a benzoic acid moiety was studied. The dye **3** is also yellow ( $\lambda_{\max}$  400 nm) in chloroform and shows a color change to blue by the addition of monoamines but a change to pink by diamines, indicating a remarkably different color based on the two ionic binding sites, carboxylate and phenolate anions, in the crown cavity.

Such a coloration ( $\lambda_{\max}$  535–800 nm) of dye crown **3**-amine complexes is related to the structure of the complex and not strongly to the relative basicity of the

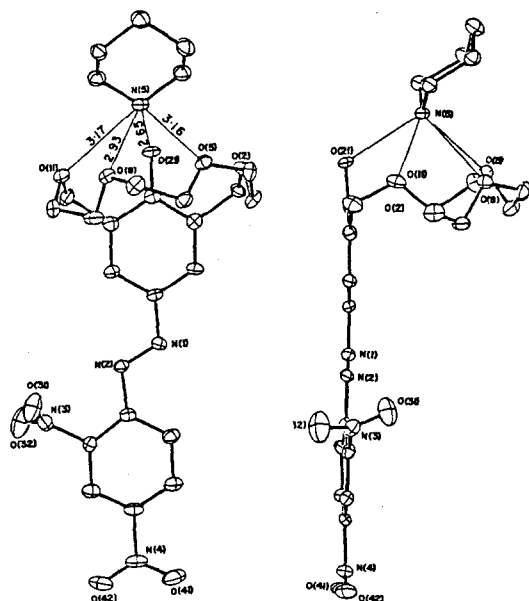


Fig. 3. ORTEP views of  $1_1$ -piperidine (1:1) complex.

amines. From the study of the relationship between the positions of absorption maxima and the concentrations of amines, it was observed that the dye **3** forms a 1 : 1 complex with some equivalents of diamine (0.5–500 eq. in the case of piperazine) and a 1 : 2 complex with a large excess of diamine (more than 500 eq. for piperazine) (Figure 4). Especially, piperazine forms a 1 : 1 complex in quantitative yield.

The molecular structure of the complex was determined by X-ray crystallography. As shown in Figure 5, the diprotonated piperazine is sandwiched between phenolate and benzoate planes in the chair form, and is bound by markedly short hydrogen bonds. This is the first example of the X-ray analysis of a crown ether-sec. amine complex, to our knowledge, and the figure indicates an interchange hydrogen bond ( $O \cdots H-N^+$ ) to be useful to bind the guest ion as well as ion-dipole interaction and hydrogen bonding.

(2.3) As an application of amine selective complexation, it was observed that the substitution pattern of amines, i.e. primary, secondary, and tertiary, may be discriminated by combined use of two azophenol hosts, pyridine- $O_4$ -crown **2** and  $O_4$ -podand **6** ( $n = 1$ ).

Dye crown **2** reacts with all kinds of amines in acetonitrile to form ammonium phenolates. The absorption maxima of 2-prim. amine systems appear in the region of 574–586 nm, which is definitely distinct from those of sec. and tert. amine systems ( $\lambda_{\max}$  602–606 nm except for dimethylamine, 592 nm) as shown in Figure 6.

On the other hand, azophenol  $O_4$ -podand **6** ( $n = 1$ ) shows the complexation-coloration with prim. and sec. amines, included sterically bulky amines such as *t*-BuNH<sub>2</sub>, (*i*-Pr)<sub>2</sub>NH, and 2,2,6,6-tetramethylpiperidine. Consequently, the combined use of two types of azophenol hosts, **2** and **6**, is highly useful to discriminate the substitution pattern of amines by means of coloration. The two end hydroxyl groups in the dyed podands are required for such discrimination of the amine pattern because no complexation-coloration is observed by addition of various amines when the hydroxyl groups are substituted with methoxyl groups.

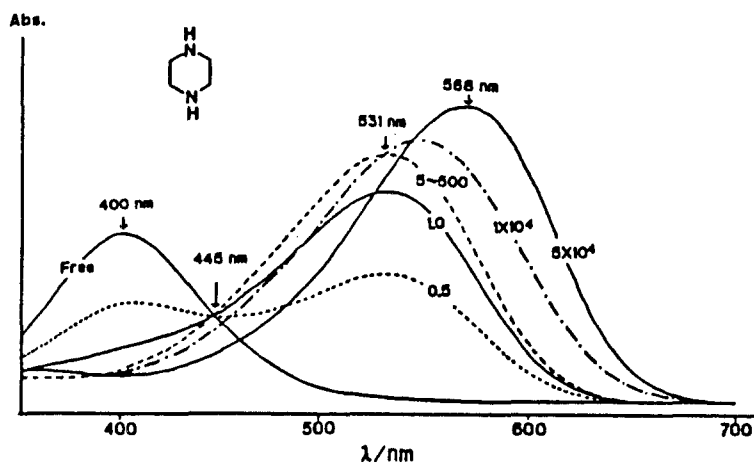


Fig. 4. Visible spectra of dye **3**-piperazine system in  $CHCl_3$ .

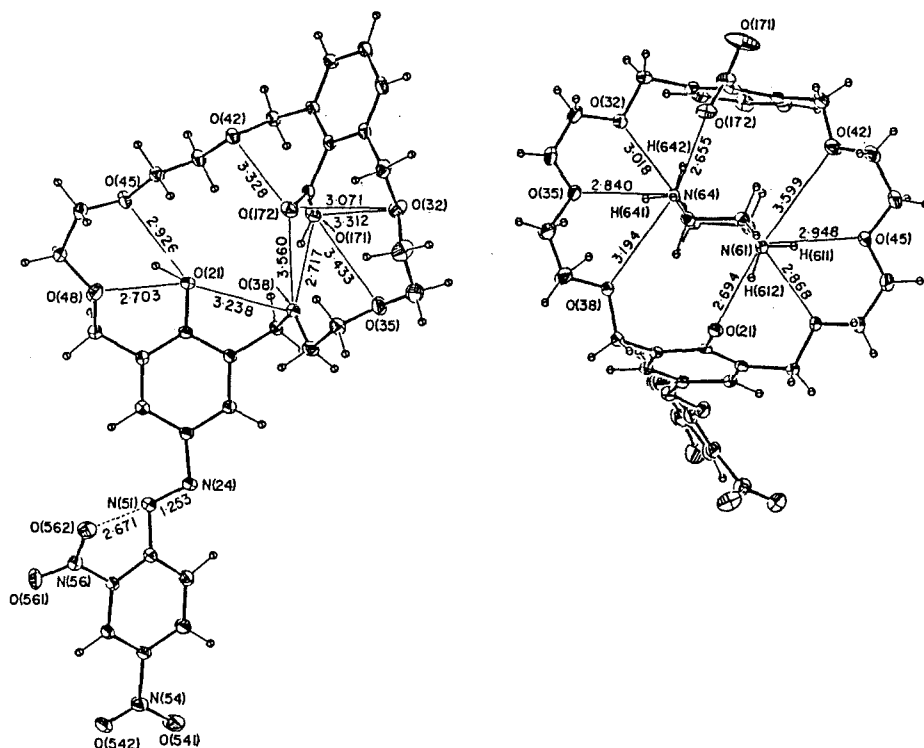


Fig. 5. ORTEP views of dye 3 (left) and 3-piperazine (1 : 1) complex (right).

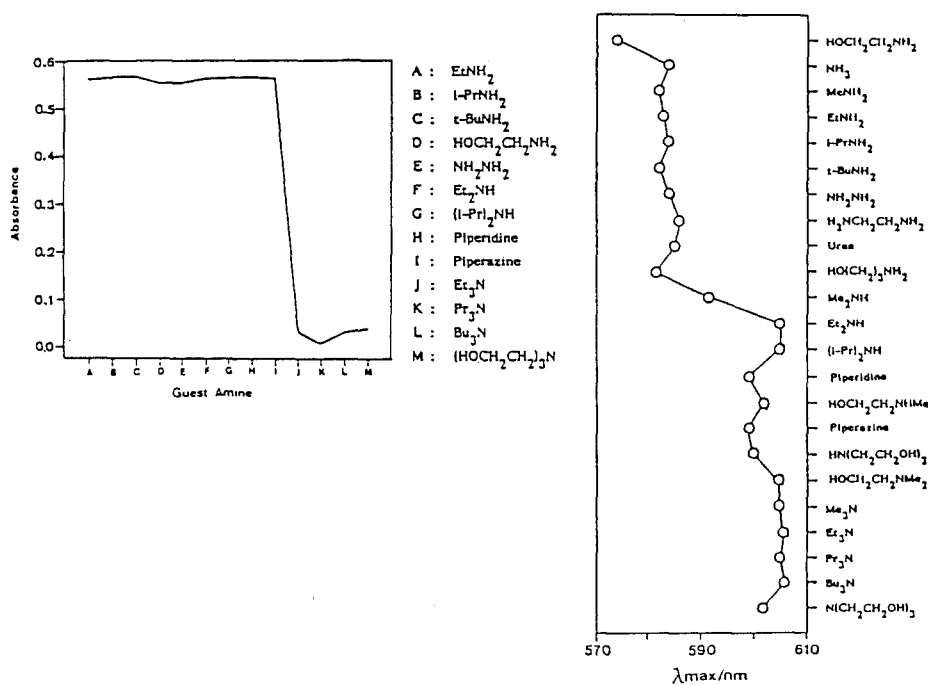
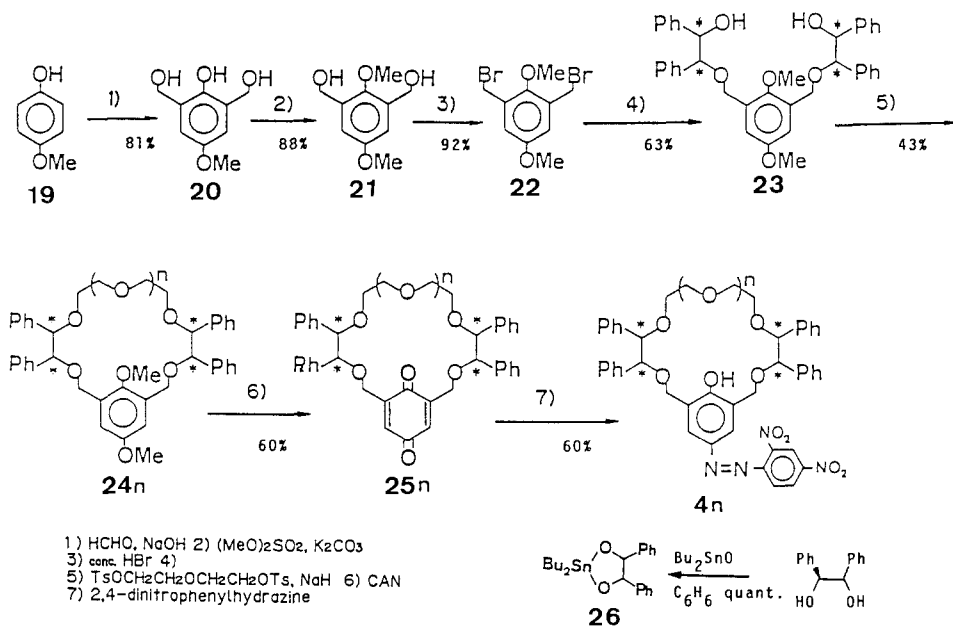


Fig. 6. Absorbances at absorption maxima of 6<sub>1</sub>-amine complexes in CHCl<sub>3</sub> (left) and absorption maxima of 2-amine complexes in CH<sub>3</sub>CN (right).



Scheme 2.

(2.4) Enantiomer selective coloration of optically active amines, our important project, was realized by chiral azophenol crown **4** incorporated with two units of optically active hydrobenzoin. The synthetic route is shown in Scheme 2. Reaction of 2,6-bis(bromomethyl)-1,4-dimethoxybenzene **22**, which is derived from hydroquinone monomethylether **19** by a three-step procedure, with the dibutyltin derivative **26** of optically active dihydrobenzoin gives optically active podand **23** in 63% yield. Cyclization of **23** with the ditosylate of polyethylene glycol, followed by oxidation with ceric ammonium nitrate (CAN) and treatment with dinitrophenylhydrazine, affords the desired chiral azophenol crowns **4n**.

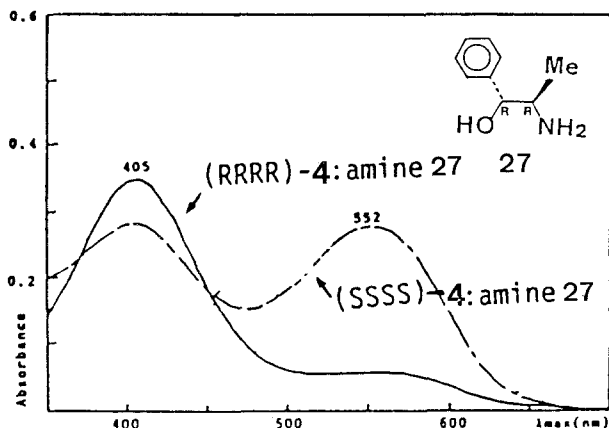
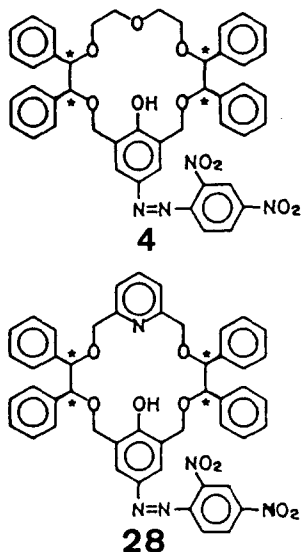
Fig. 7. Absorption spectra of dye **4**-norpseudoephedrine in chloroform.

Table I. Wavelengths (nm) and absorbances of absorption maxima in chloroform.

	4		28	
	RRRR	SSSS	RRRR	SSSS
(R)-29	567.9 0.5105	571.9 0.3605	573.9 0.5548	576.9 0.445
(S)-29	571.9 0.3860	567.0 0.5631	578.9 0.4666	573.9 0.5248
(R)-30	566.9 0.4190	569.9 0.2530	569.9 0.5012	577.0 0.3744
(S)-30	572.0 0.2475	566.9 0.4454	576.9 0.3984	569.8 0.4864
27	561.0 0.2566	553.0 0.5820	570.0 0.4341	553.0 0.5726



Of several active monoalkylamines and ethanolamines, a selective coloration with norpseudoephedrine,  $\text{Ph}(\text{OH})\text{CH}-\text{CH}(\text{NH}_2)\text{CH}_3$ , is described as a typical example. The examination with CPK molecular models shows that norpseudoephedrine **27** having the *R,R*-configuration may form a more stable complex with (*SSSS*)-dye **4**, compared to that with (*RRRR*)-dye **4**. In fact, (*RRRR*)-**4** in chloroform was kept yellow by addition of the amine in a range of concentrations,  $4.8 \times 10^{-7}$  to  $1.2 \times 10^{-6}$  M, whereas (*SSSS*)-**4** revealed a color change of the solution from yellow to reddish violet with the same concentration of the amine (Figure 7). We also observed a few examples of enantiomer selective coloration with optically active amines and some chiral dyed crowns as shown in Table I. Further study with various amines is now in progress.

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