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Photoresponsive Crown Ethers. 19. Photocontrol of Reversible Association-Dissociation Phenomena in "Tail(Ammonium)-Biting" Crown Ethers

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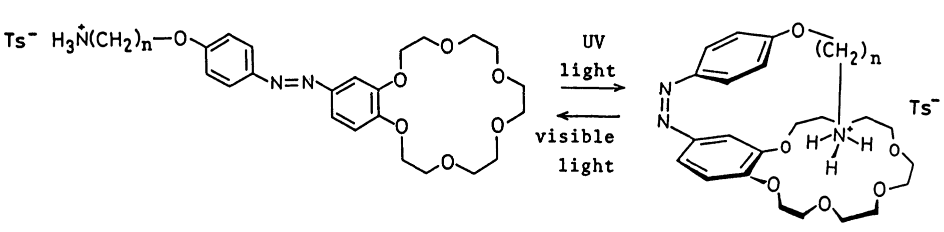
The aggregation properties of photoresponsive crown ethers (**1**) having a crown ring and an ammonioalkyl (H_3N^+-$(CH_2)_n$-, n=4, 6, 10) group attached to the two sides of an azobenzene have been evaluated through the measurements of average molecular weights and electric conductance. Osmometric determination of average molecular weights established that all trans-isomers (*trans*-**1** (n=4, 6, 10)) form the pseudo-cyclic dimers due to intermolecular crown-ammonium complexation. Photoisomerized *cis*-**1** (n=6) and *cis*-**1** (n=10), which have been designed so that intramolecular "biting" of the ammonio group to the crown can occur upon photoisomerization, existed as the discrete monomers. On the other hand, *cis*-**1** (n=4), which cannot form the intramolecular "tail-biting" complex because of the short tetramethylene spacer, existed as the pseudo-cyclic dimer. This difference was well reflected by electric conductance: in **1** (n=6) and **1** (n=10), the conductance increased synchronously with trans-to-cis photoisomerization and decreased with cis-to-trans photoisomerization. Such a photoresponsive conductance change was scarcely detected for **1** (n=4). Furthermore, the additives which enforce dissociation of the dimeric species to the monomeric species suppressed the magnitude of the photoinduced conductance change. This is a novel example that the light energy is transmitted to the conductance change.

The development of photofunctional systems which change their chemical and physical properties in response to photoirradiation is currently a focal interest in the fields of biomimetic chemistry.[1)] The photofunctional systems reported so far are related to the photocontrol of ion permeability,[2–6)] solution pH,[7,8)] membrane potentials,[9–12)] polymer conformations,[13–16)] binding to host molecules,[17–20)] etc. In these intriguing fields, the purpose of our investigation has been to control the functions of a crown ether family by an on-off light switch, which would eventually lead to the photocontrol of ion-extraction and membrane transport.[1)] Recently, we reported novel photoresponsive crown ethers (**1**) having a crown ether ring and an ammonioalkyl [-$(CH_2)_nNH_3^+$] group attached to the two sides of an azobenzene.[21)] These photoresponsive crown ethers have been designed so that intramolecular "biting" of the crown to the tail(ammonium) group can only occur upon photoisomerization of the azobenzene segments to the cis-configuration (Scheme 1: Ts^-, *p*-toluenesulfonate). We found that this "tail-biting" really occurs in *cis*-**1** (n=6) and *cis*-**1** (n=10) but in *cis*-**1** (n=4) the tetramethylene spacer is too short to allow intramolecular "tail-biting".[21)]

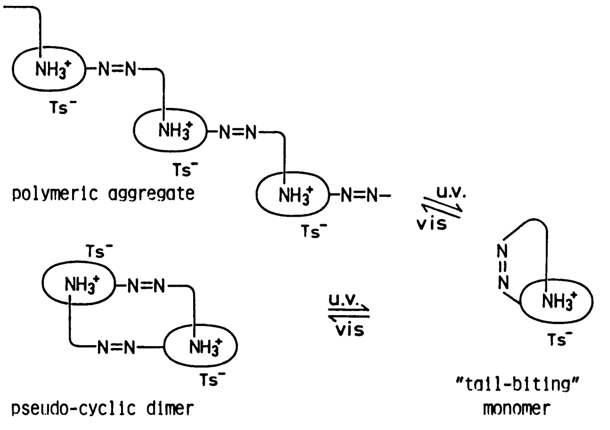
Through this study we noticed that *trans*-**1** might not be monomeric but form polymeric aggregates or pseudo-cyclic oligomers due to intermolecular crown···NH_3^+ complexation.[21)] This idea arised from the fact that K^+ ion is transported across a liquid membrane against its concentration gradient from a basic aqueous phase to an acidic aqueous phase even in the dark although the transport efficiency is much improved by UV light irradiation.[21)] This suggests that K^+ ion is released to the acidic aqueous phase because of the competitive binding with the ammonio group in *trans*-**1**.[22,23)] Since the intramolecular crown-NH_3^+ complexation is sterically impossible in *trans*-**1**, this phenomenon can be rationalized only by the intermolecular crown-NH_3^+ complexation. If this is the case, UV light irradiation which mediates trans-to-cis isomerization of the azo segment and thus facilitates intramolecular "tail-biting" should enforce the dissociation of the intermolecular complex to the intramolecular one. To obtain an insight into the photoresponsive change in the aggregation properties of **1**, we assessed the effect of photoirradiation on the electric conductance and the average molecular weight. As a working hypothesis, we considered two possible aggregation modes, polymeric aggregates and pseudo-cyclic (e.g., dimeric) oligomers (Scheme 2). **2** and **3** were used as reference compounds.



trans-**1**

cis-**1**

Scheme 1.



Scheme 2.

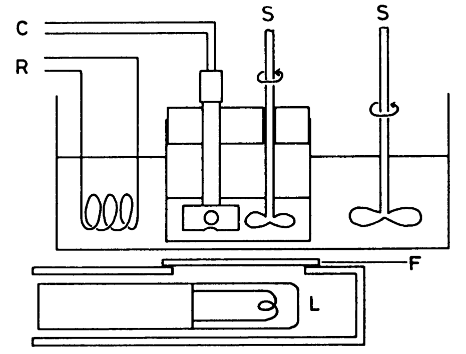
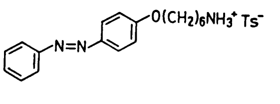


Fig. 1. Apparatus for measurements of the photoinduced conductance change. L: High-pressure Hg lamp, F: colored glass filter, S: stirrer, C: conductance electrode, R+ thermo-regulator.

Table 1. Average Aggregation Numbers (N_{av}) of *trans*-**1** and *cis*-**1**[a)]

Crown ether	Concentration g dm^{-3}	cis%[b)]	N_{av}
trans-**1**(*n*=4)	0.370	—	2.3±0.3
cis-**1**(*n*=4)	0.370	76→53	2.3±0.2
trans-**1**(*n*=6)	0.380	—	2.3±0.2
cis-**1**(*n*=6)	0.380	85→80	1.1±0.1
trans-**1**(*n*=10)	0.410	—	1.9±0.1
cis-**1**(*n*=10)	0.410	72→50	1.2±0.1

a) 50 °C, 1-butanol. b) The values indicate the cis% before and after the measurement of vapor pressure.



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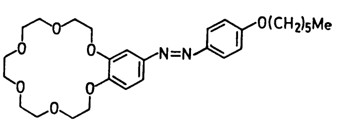

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Experimental

Materials. Preparations of 4′-[*p*-(4-aminobutoxy)phenylazo]benzo-18-crown-6, 4′-[*p*-(6-aminohexyloxy)phenylazo]benzo-18-crown-6, and 4′-[*p*-(10-aminodecyloxy)phenylazo]benzo-18-crown-6 were described previously.[21)] Treatment of these amines with an equimolar amount of *p*-toluenesulfonic acid gave *trans*-**1** (*n*=4), *trans*-**1** (*n*=6), and *trans*-**1** (*n*=10), respectively, in quantitative yields.

4-(6-Aminohexyloxy)azobenzene. 4-Hydroxyazobenzene (5.38 g; 27.1 mmol) and *N*-(6-bromohexyl)phthalimide (8.18 g; 26.4 mmol) was heated at 100 °C in 150 ml of dimethyl sulfoxide in the presence of K_2CO_3 (1.92 g; 13.9 mmol). After 11 h, the reaction mixture was poured into excess water. The aqueous solution was extracted with chloroform, the chloroform solution being dried over Na_2SO_4. After filtration, the solution was evaporated in vacuo to dryness. The residue was washed with aqueous NaOH solution to remove unreacted 4-hydroxyazobenzene. Recrystallization of the orange powder from acetonitrile gave *N*-[6-[*p*-(phenylazo)phenoxy]hexyl]phthalimide: Mp 113—114 °C, yield 39%. IR (KBr) $\nu_{\text{c-o-c}}$ 1260 cm^{-1}; $\nu_{\text{c=o}}$ 1700 and 1770 cm^{-1}. Found: C, 73.64; H, 5.83; N, 9.92%. Calcd for $C_{26}H_{25}N_3O_3$: C, 73.05; H, 5.89; N, 9.38%.

Treatment of *N*-[6-[*p*-(phenylazo)phenoxyl]hexyl]phthalimide with hydrazine hydrate in ethanol gave 4-(6-aminohexyloxy)azobenzene. The method was described previously.[21)] Mp 108—109 °C, yield 100%. It was very difficult to obtain good elemental analysis data because this compound readily absorbed CO_2 to form the carbonate. A similar behavior was observed previously for the free amines of **1**.[21)] Found: C, 70.69; H, 7.66; N, 13.80%. Calcd for $C_{18}H_{23}N_3O\cdot0.5H_2CO_3$: C, 70.87; H, 7.64; N, 13.65%. Treatment of 4-(6-aminohexyloxy)azobenzene with an equimolar amount of *p*-toluenesulfonic acid gave **2** in quantitative yield.

4′-(*p*-Hexyloxyphenylazo)benzo-18-crown-6 (3). Sodium salt of 4′-(*p*-hydroxyphenylazo)benzo-18-crown-6[21)] (0.30 g; 0.66 mmol) and 1-bromohexane (0.88 g; 3.3 mmol) was heated at 100 °C in 50 ml of dimethyl sulfoxide in the presence of K_2CO_3 (0.2 g). The progress of the reaction was monitored by a TLC method (silica gel, chloroform–methanol (10:1 v/v)). After 5 h, the reaction mixture was poured into excess water. The aqueous solution was extracted with chloroform. After evaporating the chloroform solution to dryness, the residue was recrystallized from chloroform–ligroine; mp 115—117 °C, yield 50%. IR (KBr) $\nu_{\text{c-o-c}}$ 1120 and 1250 cm^{-1}; $\nu_{\text{N=N}}$ 1500 cm^{-1}. Found: C, 65.11; H, 7.92; N, 5.09%. Calcd for $C_{28}H_{40}N_2O_7$: C, 65.10; H, 7.80; N, 5.42%.

Photoisomerization and Measurements of Electric Conductance. Trans-cis isomerization was carried out at 30 °C by using a 100W high-pressure Hg lamp with a colored glass filter: Toshiba UV-D35 ($330<\lambda<380$ nm) for UV light and Toshiba Y-46 ($\lambda>460$ nm) for visible light.

Conductance measurements were carried out at 30 °C by using an apparatus illustrated in Fig. 1. The containers for a thermostatted water-bath and a sample solution were made of transparent Pyrex glass. The sample solution was photoirradiated from the bottom of the water bath by a Hg lamp through a colored glass filter. In order to avoid the heat effect of the Hg lamp on electric conductance, both the water-bath and the sample solution were stirred effeciently.

Measurements of Average Molecular Weights. The average molecular weights (MW_{av}) of *trans*-**1** and *cis*-**1** were determined by vapor pressure osmometry[24–26] (1-butanol at 50 °C). The apparatus (Corona, Type 117) was first calibrated by compound **2** and then used for the measurement of *trans*-**1**. On the other hand, the measurement of *cis*-**1** is more complicated: The 1-butanol solution of *trans*-**1** was irradiated by UV light and the cis% at the photostationary state was determined spectrophotometrically. This solution was immediately set up in the apparatus. After the measurement of MW_{av} (about 15 min), the cis% was determined again spectrophotometrically. The results are summarized in Table 1.

Results and Discussion

Osmometric Determination of MW_{av}. It is well-established that 18-crown-6 and its analogs can form stable complexes with ammonium cations, the stability being comparable with that of the K^+ complexes.[27–30] Thus, they are frequently employed as receptors to fix the ammonium moiety in guest molecules. The detailed studies have been reported by Sutherland, Lehn, and others.[27–34] For example, bis(crown ethers) and polymethylene-α,ω-diammonio cations can form pseudo-cyclic 1:1 complexes when the distance between the two crown systems is close to the distance between the two ammonium cations.[31–34] On the other hand, intermolecular, polymeric complexes result when the two crown systems are not located suitably to form pseudo-cyclic 1:1 complexes.[31,34]

It is sterically impossible for *trans*-**1** to form the intramolecular complex between the ammonium tail and the crown ring. Therefore, it should form either polymeric aggregates or pseudo-cyclic oligomers. In *cis*-**1**, on the other hand, examination of Corey–Pauling–Koltun models suggests that introduction of a proper spacer between the ammonium tail and the crown ring allows the intramolecular complexation and that the hexamethylene group optimizes the interaction. This means that *cis*-**1** (n=6) has the potential capability to form the intramolecular "tail-biting" complex.

The average aggregation numbers ($N_{av}=MW_{av}/MW$ of monomer) were calculated from MW_{av} determined by vapor pressure osmometry (Table 1). As the cis% at the photostationary state cannot be enhanced up to 100%, the N_{av} values for *cis*-**1** imply the cis-rich mixtures. It is clearly seen from Table 1 that all trans-forms give $N_{av}=2.0\pm0.3$. This suggests that they favorably form the pseudo-cyclic "dimers" but not the polymeric aggregates. It is not yet clear why the pseudo-cyclic dimers are more energetically-favorable than the polymeric aggregates. In the polymeric aggregates (Scheme 2) the terminal ammonium cation always remains uncomplexed. In contrast, the uncomplexed cation no longer exists in the cyclic forms. The polymeric aggregates may not be formed in the solution state because of this disadvantage.

When the trans-forms were photoisomerized to the corresponding cis-forms, the N_{av} values for **1** (n=6) and **1** (n=10) decreased very close to unity, 1.1±0.1. The finding supports that the cis-forms of **1** (n=6) and **1** (n=10) exist mainly as "monomers" in solution. In other words, the intramolecular "tail-biting" really occurs and the pseudo-cyclic dimers are dissociated into the discrete monomers. This is reasonably explained by the cis-configuration of the azo segment which facilitates the intramolecular "tail-biting" sterically. In contrast, the N_{av} for **1** (n=4) was scarcely affected by photoirradiation. The difference is readily ascribed to the incapability of *cis*-**1** (n=4) to bite at the intramolecular ammonium tail. One can conclude, therefore, that in **1** (n=4) not only the trans-form but also the cis-form should form the pseudo-cyclic dimers in solution.

Photoresponsive Conductance Change. Electric conductance is defined as a function of mobility of charged particles in solution. Therefore, it should reflect the photoinduced change in the molecular size. First, we examined the photoirradiation effect on **1** (n=6) in 1-butanol which was used for the determination of MW_{av} (Fig. 2). Very interestingly, the conductance ($\Lambda=7.59\ \mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ for *trans*-**1** (n=6)) increased on UV light irradiation ($330<\lambda$ 380 nm) and finally saturated at $\Lambda=8.59\ \mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$ (cis 80%). On visible light irradiation ($\lambda>460$ nm) it decreased gradually and finaly reached the Λ value for *trans*- **1** (n=6). This process could be repeated several times by alternate irradiation of UV and visible light. We found, however, that the absolute Λ values in 1-butanol were affected sensitively by a small amount of concomitant water. On the other hand, the reproducible Λ values can be obtained when the concentration of 1-butanol was reduced by mixing with aprotic solvents. We thus employed a mixed solvent of *o*-dichlorobenzene–1-butanol=(9:1 v/v) for detailed examinations.

Figure 3 shows the effect of photoirradiation on cis% and conductance. Two curves were obtained by

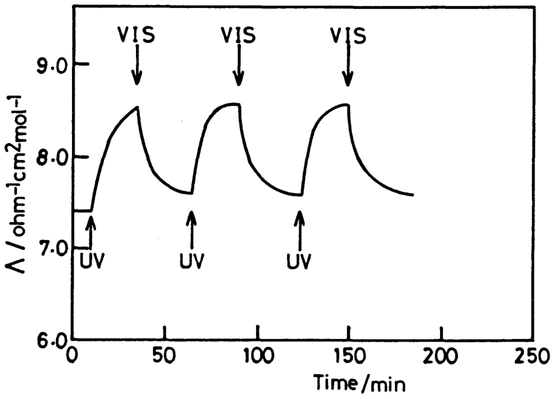


Fig. 2. Photoresponsive conductance change for **1**(n=6) in 1-butanol. [**1**(n=6)]=5.40×10^{-4} mol dm^{-3}.

using the same apparatus (Fig. 1) and the same conditions (see caption to Fig. 3). It is seen from Fig. 3 that two curves show excellent coincidence. Similar photoresponsiveness of both cis% and conductance was also observed for **1** (n=10) (Fig. 4: cis% is not illustrated here). The magnitude of the conductance change ($\Delta\Lambda$=2.00 ohm^{-1} cm^2 mol^{-1}) was somewhat greater than that for **1** (n=6) (0.85 ohm^{-1} cm^2 mol^{-1}). When visible light was not irradiated, the thermal cis-to-trans isomerization took place slowly. The first-order rate constants (k) determined at 30 °C by following the appearance of the absorption maxima of *trans*-(**1**) (364—368 nm)[21] were 2.39×10^{-5} s^{-1} for **1** (n=6) and 8.90×10^{-5} s^{-1} for **1** (n=10). The k values in the dark could be also determined by following the slow decrease in the conductance; k=2.30×10^{-5} s^{-1} for **1** (n=6) and 8.65×10^{-5} s^{-1} for **1** (n=10). Several lines of excellent coincidence between the spectroscopic data and the conductance data support that the conductance change is caused by the photoinduced trans-cis isomerization. In other words, the monomeric cis-forms have the Λ value higher than the dimeric trans-forms and two aggregation modes can be rever-

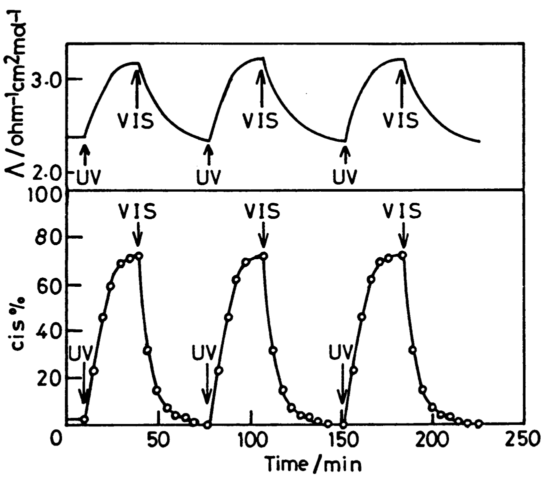


Fig. 3. Photoresponsive conductance change and cis% change for **1**(n=6) in *o*-dichlorobenzene-1-butanol=9:1 (v/v). [**1**(n=6)]=5.40×10^{-4} mol dm^{-3} for both conductance and cis% determination.

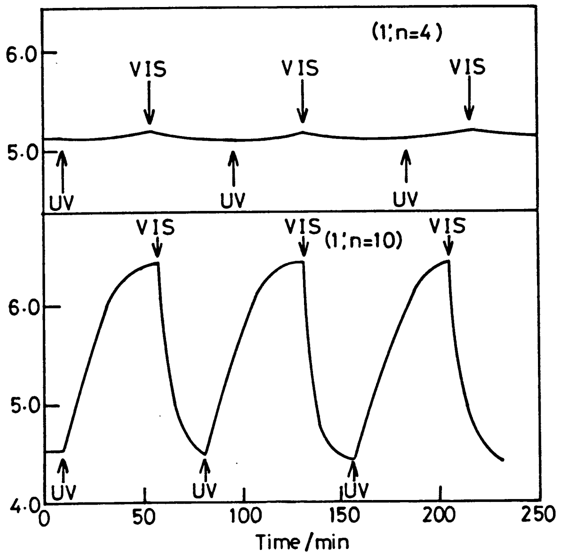


Fig. 4. Photoresponsive conductance change for **1**(n=4) and **1**(n=10) in *o*-dichlorobenzene-1-butanol=9:1 (v/v). [**1**(n=4)]=5.57×10^{-4} mol dm^{-3}, [**1**(n=10)]=5.39×10^{-4} mol dm^{-3}.

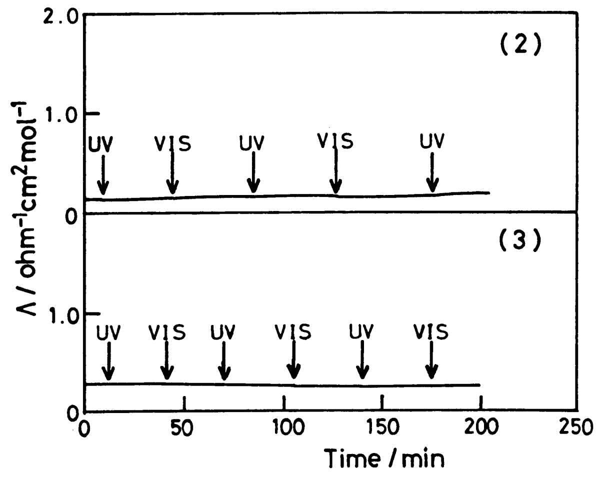


Fig. 5. Photoresponsive conductance change for **2** and **3** in *o*-dichlorobenzene-1-butanol=9:1 (v/v). [**2**]=5.45×10^{-4} mol dm^{-3}, [**3**]=5.36×10^{-4} mol dm^{-3}.

Table 2. Influence of Photoirradiation on Electric Conductance of **1**[a)]

Conductance ohm^{-1} cm^2 mol^{-1}	Additive (concd mmol dm^{-3})	**1**(n=4)	**1**(n=6)	**1**(n=10)
Λ_{dark}[b)]	—	5.08	2.34	4.43
Λ_{light}[c)]	—	5.16	3.19	6.43
$\Delta\Lambda$[d)]	—	0.08	0.85	2.00
$\Delta\Lambda$[d)]	18-Crown-6 (5.00)	—	0.11	—
$\Delta\Lambda$[d)]	$C_{12}H_{25}OSO_3^-K^+$ (0.56)	—	0.26	—
$\Delta\Lambda$[d)]	$CH_3NH_3^+Ts^-$ (21.3)	—	0.48	—

a) 30 °C, *o*-dichlorobenzene-1-butanol=9:1 (v/v). b) Electric conductance in the dark. c) Maximum electric conductance under UV light irradiation. cis% at the maximum conductance: 58% for **1**(n=4), 72% for **1**(n=6), and 78% for **1**(n=10). d) $\Delta\Lambda=\Lambda_{\mathrm{light}}-\Lambda_{\mathrm{dark}}$.

sibly interconverted by photoirradiation. The finding would be rationalized in terms of the difference in the mobility between the monomeric species and the dimeric species.

In contrast, the conductance change was scarcely detected for **1** (n=4) which could not form the "tail-biting" monomeric complex. Reference compounds, **2** and **3**, which have neither a crown ring nor an ammonium tail, showed no conductance change although the trans-cis photoisomerization really occurred in the conductance cell (maximum cis% under UV light irradiation, 51% for **2** and 58% for **3**: Fig. 5). As a summary of the foregoing results (Table 2), one can draw a conclusion that the photoinduced conductance change is observed only for the "tail-biting" crown ethers which can realize reversible interconversion between the monomeric form and the pseudo-cyclic, dimeric form.

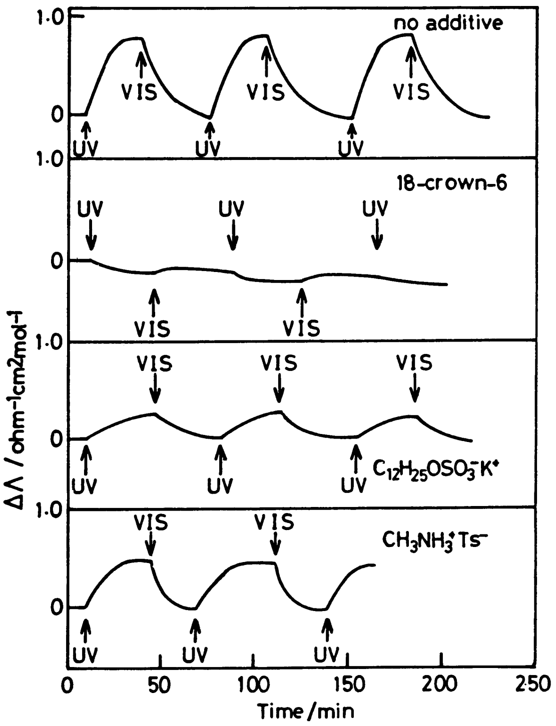


Fig. 6. Effect of additives on the photoresponsive conductance change for [**1**(n=6)] (5.40×10^{-4} mol dm^{-3}) in *o*-dichlorobenzene-1-butanol=9:1 (v/v). [18-Crown-6]=5.00×10^{-3} mol dm^{-3},[$C_{12}H_{25}OSO_3^-K^+$]=5.60×10^{-4} mol dm^{-3}, [$CH_3NH_3^+Ts^-$]=2.13×10^{-2} mol dm^{-3}.

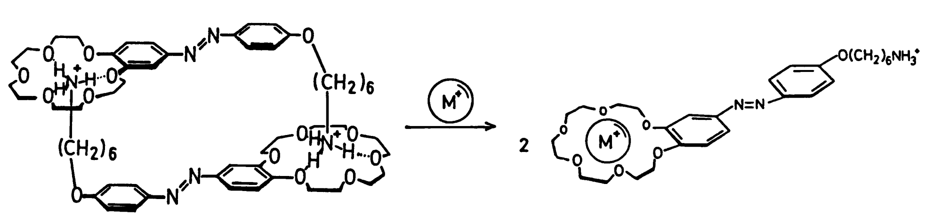
Effects of Additives. In solvent extraction with **1** (n=6), we found that *trans*-**1** (n=6) can extract K^+ into the organic phase while *cis*-**1** (n=6) has almost no metal affinity.[21] On the other hand, the present study has established that both *trans*- and *cis*-**1** (n=6) form the complexes with the ammonio groups. The difference in the K^+ affinity should be related to the stability of the ammonium complexes: That is, the intermolecular ammonium cation in *trans*-**1** (n=6) can be replaced competitively by K^+, whereas the intramolecular ammonium-crown complex in *cis*-**1** (n=6) is so stable that the ammonium cation binds to the crown cavity in preference to K^+. This suggests that the added K^+ ion would selectively dissociate the dimeric aggregates of *trans*-**1** (n=6).

Figure 6 indicates the influence of K^+ and $CH_3NH_3^+$ on the photoresponsive wave of **1** (n=6). Separately, we confirmed that the cis% is scarcely affected by the addition of these ions. It is clearly seen from Fig. 6 that the photoresponsive wave for **1** (n=6) becomes significantly smaller in the presence of potassium dodecyl sulfate and methylammonium *p*-toluenesulfonate (Table 2). The finding suggests that these cations can dissociate the pseudo-cyclic dimers into the monomers through competitive binding to the crown cavity (Scheme 3).

Similar suppression of the conductance change can be induced by the additive which selectively interacts with the ammonio group. For instance, addition of 18-crown-6 effectively suppressed the photoinduced conductance change (Fig. 6). Conceivably, added 18-crown-6 competes with the crown ring in **1** for the ammonio group. As a result, the pseudo-cyclic dimers would be dissociated into the monomers.

Conclusions

The present study demonstrated that the conductance of the solution containing **1** (n=6) and **1** (n=10) changes reversibly in response to photoirradiation. The novel phenomenon is ascribed, on the basis of several lines of experimental evidence, to photoinduced association-dissociation phenomena in the "tail(ammonium)-biting" crown ethers. Since the conductance change is sensitively affected by added K^+, ammonium ions, etc., the concept may be applicable more generally to interdisciplinary fields between photochemistry and electrochemistry including sensors, membrane systems, etc.



Scheme 3.

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