SYNTHESIS AND PHOTOSWITCHABLE COMPLEXATION/ EXTRACTION PROPERTIES OF LIPOPHILIC AZOBIS(BENZO-15-CROWN-5) IONOPHORES FOR ALKALI METAL CATIONS†

Kazunori Odashima,*[,a] Koji Tohda,[b] Shinji Yoshiyagawa,[c] Shinichiro Yamashita,[c] Masamitsu Kataoka,[c,§] and Yoshio Umezawa*[,b]

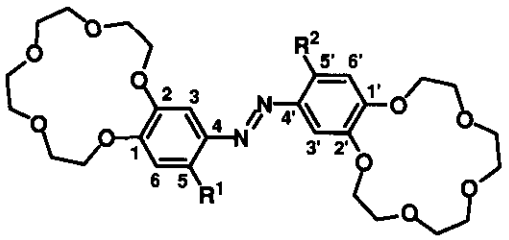
[a] Graduate School of Pharmaceutical Sciences, The University of Tokyo, Bunkyo-Ku, Tokyo 113, Japan [b] Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-Ku, Tokyo 113, Japan [c] Department of Chemistry, School of Science, Hokkaido University, Kita-Ku, Sapporo 060, Japan [§] Present address: Otaru University of Commerce, Otaru-Shi, Hokkaido 047, Japan

Abstract – Novel lipophilic derivatives of azobis(benzo-15-crown-5) (**1b**, **1c**) were synthesized and their photoisomerization, complexation and extraction properties for alkali metal cations were investigated. Upon UV light irradiation, the photostationary state of the *trans* and *cis* isomers was reached and, with both **1b** and **1c**, the extractabilities of Rb^+ and Cs^+ increased due to the formation of 1:1 sandwich-type complexes by the *cis* isomers. On the other hand, the extractability of K^+ decreased, possibly because the 2:1 complexes formed by the *trans* isomers are more stable and/or lipophilic than the complexes of the *cis* isomers.

INTRODUCTION

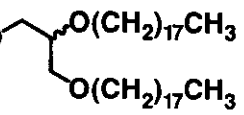
Azobis(crown ether)s, which are capable of adopting the *trans* and *cis* geometries by photoisomerization, compose a versatile class of photoswitchable ionophores that can control the complexation of metal cations by irradiation of UV or visible light.[1] Previously, Shinkai and co-workers[1a-c,2] synthesized a series of such ionophores and made extensive studies on the photocontrol of their extraction and transport properties. In the case of azobis(benzo-15-crown-5) (**1a**), the *cis* isomer forms a stable sandwich-type 1:1 complex with K^+ ion, whereas the complexation by the *trans* isomer is very weak.[2a,c] Transport of K^+ ions across a liquid membrane incorporated with **1a** was found to be accelerated by irradiation of UV light.[2a,d]

† Dedicated to Professor Koji Nakanishi, Columbia University, on the occasion of the 75th birthday for his outstanding contribution to bioorganic and natural product chemistry.



1a: $R^1 = R^2 = -H$

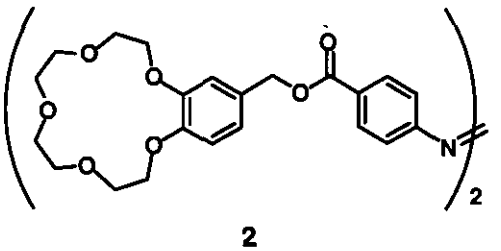
1b: $R^1 = -O(CH_2)_{17}CH_3$, $R^2 = -H$

1c: $R^1 =$  , $R^2 = -H$

1d: $R^1 = R^2 = -C(CH_3)_3$

1e: $R^1 = -(CH_2)_{11}CH_3$, $R^2 = -H$

8: $R^1 = -OH$, $R^2 = -H$



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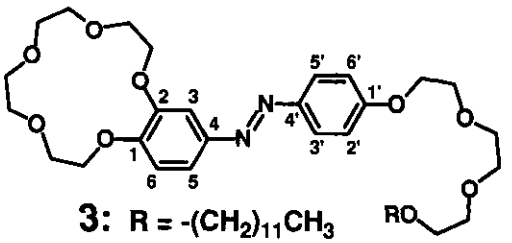
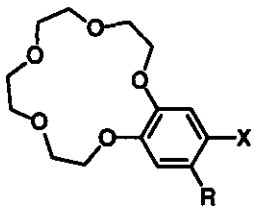


3: $R = -(CH_2)_{11}CH_3$

(The carbons of the azobisbenzene moiety are conveniently numbered.)

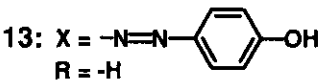


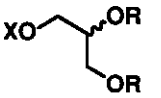
4: $X = -NH_2$, $R = -H$

5: $X = -H$, $R = -(CH_2)_{17}CH_3$

6: $X = -H$, $R = -OH$

7: $X = -NO_2$, $R = -H$

13: $X =$  , $R = -H$

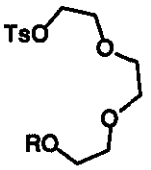


9: $X = -Ts$, $R = -(CH_2)_{17}CH_3$

10: $X = -Bn$, $R = -H$

11: $X = -Bn$, $R = -(CH_2)_{17}CH_3$

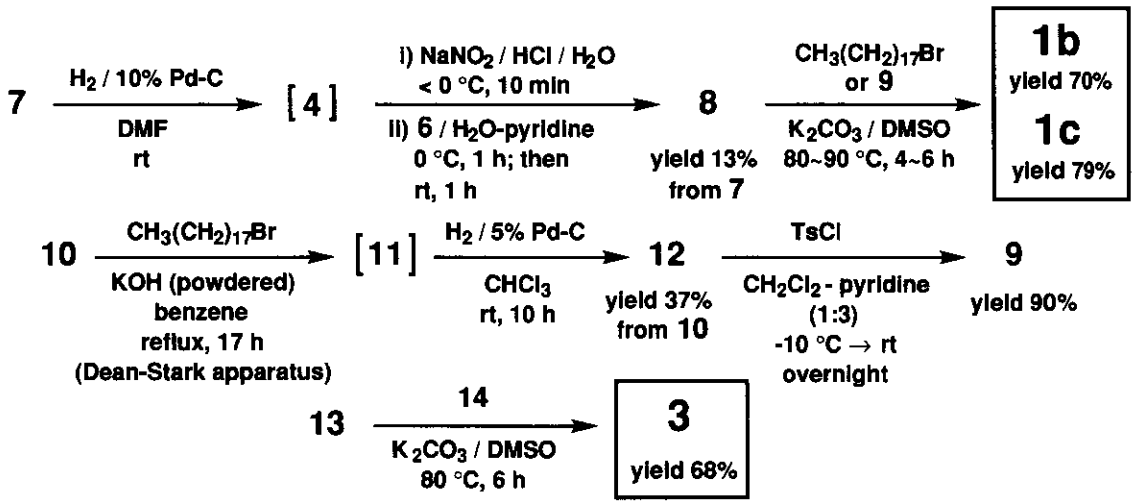
12: $X = -H$, $R = -(CH_2)_{17}CH_3$



14: $R = -(CH_2)_{11}CH_3$

More recently, Osa and co-workers[1d,e,3] investigated photoinduced changes in the membrane potential of poly(vinyl chloride) (PVC)-supported liquid membranes containing photoswitchable ionophores such as azobenzene-linked bis(crown ether)s (*e.g.*, **2**[3a]). When the membrane in contact with an aqueous solution of guest cation was exposed to UV light, a change in the membrane potential, arising from photoisomerization of the ionophore in the membrane, was observed. This work implies that photoresponsive crown ethers may serve as a molecular probe to help understanding the molecular mechanism of phase boundary potentials, provided that the photoequilibrium concentrations of the *cis* and *trans* isomers in the membrane bulk and their complexation stability constants for guest cations can be correlated with the photoinduced changes in the membrane potential. Since such a molecular probe must be completely retained in the membrane phase not only in the uncomplexed but also in the complexed state, a new type of azobenzene-linked bis(crown ether)s with high lipophilicity and defined structure must be developed.

In this paper, we describe the synthesis of azobis(benzo-15-crown-5) derivatives (**1b**, **1c**) and a reference compound (**3**), and their photoisomerization, complexation and extraction properties for alkali metal cations under UV or visible light irradiation. Compounds (**1b**) and (**1c**) are highly lipophilic derivatives of azobis(benzo-15-crown-5) (**1a**).[2] In contrast to



Scheme 1. Synthesis of **1b**, **1c** and **3** (all yields correspond to purified yields)

another type of lipophilic derivative (**1d**) having a substituent at both benzene rings,[2c] the formation of intramolecular sandwich type complexes will not be inhibited with **1b** and **1c** having a substituent at only one of the benzene rings. In addition, compared to the azobenzene-linked bis(crown ether)s of type (**2**),[3a] more distinct structural difference between the *cis* and *trans* isomers can be expected for ionophores (**1b**) and (**1c**) because, in the latter compounds, the 15-crown-5 rings are directly attached to the benzene rings of the azobenzene group.

RESULTS AND DISCUSSION

Synthesis of Azobis(benzo-15-crown-5) Derivatives and Reference Compound. Initially, we intended to synthesize the azobis(benzo-15-crown-5) derivative of type (**1e**) with a lipophilic alkyl chain introduced directly to the benzene ring. However, the diazo coupling reaction between 4'-aminobenzo-15-crown-5 (**4**) and 4'-octadecylbenzo-15-crown-5 (**5**) failed, possibly because of steric hindrance. We then chose as the target molecules the compounds of type (**1b**) and (**1c**) because the diazo coupling step in this case can be carried out with 4'-hydroxybenzo-15-crown-5 (**6**), which is much less hindered and much more activated than **5**. The synthesis of azobis(benzo-15-crown-5) derivatives (**1b**, **1c**) and reference compound (**3**) was carried out as shown in Scheme 1. 4'-Aminobenzo-15-crown-5 (**4**), prepared from 4'-nitrobenzo-15-crown-5 (**7**) by catalytic hydrogenation,[4] was diazotizated and reacted with 4'-hydroxybenzo-15-crown-5 (**6**)[5] to give the hydroxyazobis(benzo-15-crown-5) (**8**), which was alkylated with 1-bromooctadecane or (*RS*)-2,3-*O*-dioctadecylglycerol *p*-toluenesulfonate (**9**) to give target compounds (**1b**) and (**1c**), respectively. *p*-Toluenesulfonate (**9**)[6a] was prepared from **10**[6b,c] *via* **11**[6c,d] and **12**.[6a,c,d] Reference compound (**3**) was synthesized by reacting 4'-(*p*-hydroxyphenylazo)benzo-15-crown-5 (**13**)[7] with the *p*-toluenesulfonate of triethylene glycol monododecyl ether (**14**).

***Trans/Cis* Ratio in Photoisomerization.** Photoisomerization of ionophores (**1b**), (**1c**) and (**3**) between the *trans* and *cis* forms was examined in PVC-supported liquid membranes with dibutyl phthalate (DBP) as a membrane solvent. These solvent polymeric membranes are to be used as electrode membranes for potentiometric studies.[8] In the case of the membrane containing **1b**, a strong absorption band was observed at 400 nm, which is assigned to the π-π^* transition of the *trans* azobenzene chromophore. Upon UV light irradiation, the absorption maximum of the membrane decreased markedly, indicating the formation of the *cis* isomer. Photostationary state was reached within 1 min. The ratio of *cis*-**1b** at the photostationary state, which was estimated from the decrease in the absorbance at 400 nm (see the Experimental Section), was 42%. When the membrane was exposed to visible light, the original adsorption spectrum was recovered rapidly within 1 min. The *trans/cis* photoisomerization of **1b** in the PVC membrane was reversible and reproducible. The changes in the absorption spectra of **1c** and **3** in PVC membranes were similar to that for **1b**. The intensities of the absorption maxima of the *trans* azobenzene chromophores, 398 and 368 nm for **1c** and **3**, respectively, changed reversibly upon photoirradiation. The *cis* percentage of **1b**, **1c** and **3** at the photostationary state is summarized in Table 1. It should be noted that the *cis* percentages of these ionophores were almost constant regardless of the concentration of the ionophore in the membrane.

Table 1. The *Cis* Percentage of Ionophores (**1b**), (**1c**) and (**3**) at the Photostationary State in PVC-supported Liquid Membranes[a]

	cis isomer (%)		
ionophore concentration	0.01 mM	0.1 mM	1.0 mM
1b	42.0 ± 0.1[b]	41.8 ± 0.1	42.2 ± 0.3
1c	40.1 ± 0.4	39.2 ± 0.3	39.4 ± 0.4
3	50.5 ± 0.5	51.0 ± 0.4	50.1 ± 0.3

[a] Membrane composition: DBP/PVC (2:1 wt/wt) containing each concentration of ionophore. [b] Standard deviation (n = 5).

Photoinduced Changes in Extractability of Alkali Metal Cations. Complexation/extraction abilities of ionophores (**1b**), (**1c**) and (**3**) for alkali metal cations were estimated by solvent extraction of alkali metal picrates from water into DBP under UV or visible light irradiation. The extractabilities (percent extracted) are summarized in Table 2. It can be seen that the *trans* and *cis* isomers of ionophores (**1b**) and (**1c**) exhibit contrasting extraction behaviors. The extractability increased for Rb^+ and Cs^+ ions but decreased for K^+ and Na^+ ions under UV light irradiation.

Table 2. Extractabilities (Percent Extracted) of Alkali Metal Picrates with Ionophores (**1b**), (**1c**) and (**3**) under Visible and UV Light Irradiation[a]

ionophore		extracted picrate (%)			
		Na^+	K^+	Rb^+	Cs^+
1b	visible	21.8 ± 0.8[b]	32.2 ± 0.1	24.2 ± 0.6	18.4 ± 0.4
	UV	19.4 ± 0.3	28.6 ± 0.2	33.6 ± 0.2	22.3 ± 0.6
1c	visible	34.4 ± 0.3	36.7 ± 0.3	12.3 ± 0.4	13.1 ± 1.3
	UV	33.1 ± 0.5	29.2 ± 0.2	22.0 ± 0.3	21.5 ± 0.8
3	visible	37.5 ± 0.4	42.3 ± 0.3	31.2 ± 0.3	14.2 ± 0.7
	UV	35.4 ± 0.3	31.3 ± 0.2	25.0 ± 0.4	8.2 ± 1.2

[a] Organic phase [dibutyl phthalate (DBP)]: [ionophore] = 1.00×10^{-3} M. Aqueous phase: [picric acid] = 5.00×10^{-5} M, [alkali metal hydroxide] = 1.00×10^{-3} M, [alkali metal chloride] = 5.00×10^{-1} M. [b] Standard deviation (n = 3).

Previously, Shinkai and co-workers[2a,c] reported photocontrolled extraction of alkali metal cations by azobis(benzocrown ether)s with no long alkyl substituent in a *o*-dichlorobenzene/ water system. In the case of azobis(benzo-15-crown-5) (**1a**), the extractability increased for K^+, Rb^+ and Cs^+ but decreased for Na^+.[2a] They explained the increased extractabilities of K^+, Rb^+ and Cs^+ ions on the basis of the formation of sandwich-type 1:1 complexes (2:1 ratio of 15-crown-5 moiety and cation) because the diameters of these ions are greater than the cavity size of the 15-crown-5 ring. Based on this explanation, the increased extractabilities of Rb^+ and Cs^+ ions for *cis*-**1b** and *cis*-**1c** can also be ascribed to the formation of a more stable and/or lipophilic complex between the *cis* isomer and the cation.

However, the UV-induced change in the extractability of K^+ ion for ionophores (**1b**) and (**1c**) was quite opposite from that for **1a**. Ionophores (**1b**) and (**1c**) showed a decreased extractability whereas **1a** showed a much increased extractability for K^+ ion. These results contrast the expectation from the CPK molecular model that steric hindrance by the alkyl side chain of ionophore (**1b**) or (**1c**) does not interfere with the formation of a sandwich-type complex in the *cis* form. In relation to this reversed extractability, we found that the *trans* isomers of **1b** and **1c** form 2:1 host-guest complexes with $KClO_4$ in ethanol, as indicated by UV/visible titration based on a continuous variation method (Job's plot). This complexation stoichiometry suggests that the greater extractabilities of K^+ ion by the *trans* isomers of **1b** and **1c** may be due to the formation of intermolecular 2:1 sandwich-type complexes that are

even more stable and/or lipophilic than the intramolecular 1:1 sandwich-type complexes formed by the *cis* isomers. The difference in the extractability of K^+ ion between the present and the reported[2a,c] studies may arise from the higher lipophilicity of the present ionophores and/or the differences in the experimental conditions. With respect to ionophore (**3**), a decrease in the extractability upon UV light irradiation was observed for all cations examined. The reason for the lower extractability for the *cis* isomer is not obvious but the linear polyether moiety of *cis*-**3** may not contribute effectively to the formation of a sandwich-type complex.

CONCLUSION

In this study, lipophilic derivatives of azobis(benzo-15-crown-5) (**1b**, **1c**) and a reference compound (**3**) were synthesized, and their photoisomerization, complexation and extraction properties for alkali metal cations were investigated under UV or visible light irradiation. Under UV light irradiation, these ionophores underwent photoisomerization from the *trans* to the *cis* isomers by 40~50%. The extractabilities (percent extracted) of Na^+, K^+, Rb^+ and Cs^+ ions by these ionophores were determined in a dibutyl phthalate (DBP)/water system. In the case of **1b** and **1c**, an increased extractability by the formation of a 1:1 sandwich-type complex was observed for Rb^+ and Cs^+ ions. The photoequilibrium concentrations and the metal cation extractabilities of the *cis* and *trans* isomers determined in the present study will enable the estimation of the ratio of their complexation stability constants and hence enable the calculation of the number of cationic complexes at the membrane surface. The surface charge density thus calculated can be correlated with the guest-induced change in the membrane potential, and in this way the photoswitchable ionophores may serve as a molecular probe for understanding the molecular mechanism of phase boundary potentials at ion-selective PVC liquid membranes. The details will be reported elsewhere.[8]

EXPERIMENTAL SECTION

General. Melting points are uncorrected. Nuclear magnetic resonance (NMR) spectra were measured on a JMS-GX-400 [Nihon Denshi (JEOL), Tokyo, Japan] or a R-1900 (Hitachi, Tokyo, Japan) Fourier transform spectrometer. Chemical shifts are reported in δ values in ppm downfield of tetramethylsilane (TMS) as an internal standard. Coupling constants (*J*) are reported in hertz (Hz). Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Infrared (IR) spectra were recorded on a Model 1720-X Fourier transform infrared spectrophotometer (Perkin-Elmer, Norwalk, CT, U. S. A.). Mass spectra (MS; EI or FAB mode) were recorded on a JEOL JMS-HX 110, JMS-DX 303, JMS-DX 300 or JMS-01SG-2 mass spectrometer.

Materials. 4'-Hydroxybenzo-15-crown-5 (**6**)[5] was prepared according to the literature.[5a] (*RS*)-2,3-*O*-dioctadecylglycerol *p*-toluenesulfonate (**9**)[6a] was prepared from (*RS*)-1-*O*-

benzylglycerol (**10**)[6b,c] *via* **11**[6c,d] and **12**[6a,c,d] by dialkylation of **10** (1-bromooctadecane/powdered KOH/benzene; reflux, 17 h, Dean-Stark apparatus),[6c] followed by catalytic hydrogenation (H_2/5% Pd-C/$CHCl_3$; rt, 10 h; purified yield 37% from **10**) and tosylation [TsCl/CH_2Cl_2-pyridine (1:3); -10 °C → rt, overnight; purified yield 90% from **11**]. 4'-(*p*-Hydroxyphenylazo)benzo-15-crown-5 (**13**)[7] was prepared from diazotizated **4** and phenol by using the literature procedure[9] with some modification. Compound (**14**) was prepared by tosylation of triethylene glycol monododecyl ether [TsCl/CH_2Cl_2-pyridine (1:3); -10 °C → rt; purified yield 29%]. Dibutyl phthalate (DBP; 021-06936; Wako Pure Chemical, Osaka, Japan) was purified by distillation under reduced pressure (bp_7 188 °C). Poly(vinyl chloride) (PVC; $n_{av} \approx 1100$; 223-00255) was purchased from Wako Pure Chemical and used without further purification. The following inorganic salts were of the highest quality grade available from Wako Pure Chemical and used without further purification: NaCl (191-01665), KCl (163-03545), RbCl (187-00321), CsCl (035-01952). Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under argon. *p*-Toluenesulfonyl chloride (TsCl) was purified by recrystallization from hexane. 1-Bromooctadecane was purified by distillation under reduced pressure (bp_{12} 214-216 °C). Pyridine was distilled from and stored over KOH. *N,N*-Dimethylformamide (DMF, bp_{23} 58°C) and dimethyl sulfoxide (DMSO, bp_{14} 84°C) were distilled under reduced pressure. Deionized and charcoal-treated water (>17.5 MΩ cm specific resistance), obtained by a Milli-Q Type I reagent grade water system (Millipore, Bedford, MA, U. S. A.), was used for all measurements.

Synthesis of Azobis(benzo-15-crown-5) Derivatives and Reference Compound. Hydroxyazobis(benzo-15-crown-5) (8). 4'-Nitrobenzo-15-crown-5 (**7**) (0.60 g, 1.9 mmol) was converted to 4'-aminobenzo-15-crown-5 (**4**) by catalytic hydrogenation according to the literature procedure (H_2/10% Pd-C/DMF; rt).[4] The crude product was dissolved in 7.5 M HCl (0.80 mL, 6.0 mmol) and cooled below 0 °C with an ice-salt bath. To this solution was added a cooled aqueous solution of $NaNO_2$ (0.13 g in 5 mL water, 1.9 mmol) dropwise over a period of 10 min. After excess HNO_2 was trapped by addition of urea, the mixture was neutralized by careful addition of solid Na_2CO_3. Then, under ice cooling, a cooled solution of 4'-hydroxybenzo-15-crown-5 (**6**) (0.54 g, 1.9 mmol) in pyridine (2 mL) was added, and the reaction mixture was stirred for 1 h in an ice bath and further for 1 h at rt. The reaction mixture was poured carefully into a mixture of conc HCl (5 mL) and ice (30 g), and the mixture was extracted with $CHCl_3$ after the ice melted. The residue obtained after usual workup was purified by column chromatography [silica gel; CH_2Cl_2-MeOH (95:5)], followed by recrystallization from EtOH to give analytically pure **8** as a red powder (0.14 g, 13%): mp 179 °C. ^{1}H-NMR [CD_3OD-CCl_4 (1:9)] δ 3.6-4.3 [32 H, m, O(CH_2)$_2$O], 6.4-7.5 (5 H, m, Ar*H*). MS *m/z* 578 (M^+). *Anal.* Calcd for $C_{28}H_{38}N_2O_{11}\cdot 0.5H_2O$: C, 57.23; H, 6.69; N, 4.77. Found: C, 57.46; H, 6.54; N, 4.61.

Azobis(benzo-15-crown-5) Ionophore (1b). A suspension of hydroxyazobis(benzo-15-crown-5) (**8**; 58 mg, 0.10 mmol), 1-bromooctadecane (0.17 g, 0.50 mmol) and K_2CO_3 (0.1

g, 0.7 mmol) in DMSO (30 mL) was stirred at 80-90 °C for 4 h. The reaction mixture was cooled to rt and extracted with $CHCl_3$ (100 mL). The ocher solid obtained after usual workup was purified by recrystallization from EtOH to give analytically pure **1b** as a yellow powder (58 mg, 70%): mp 111-113 °C. ^{1}H-NMR ($CDCl_3$) δ 0.88 (3 H, t, J = 6.8 Hz, CH_3), 1.25 [28 H, br s, $CH_3(CH_2)_{14}(CH_2)_3O$], 1.52 [2 H, quintet, J = 7.0 Hz, $CH_2CH_2(CH_2)_2O$], 1.86 (2 H, quintet, J = 7.0 Hz, $CH_2CH_2CH_2O$), 3.75-3.80 [16 H, m, $ArO(CH_2)_2O(CH_2)_2$], 3.88-3.97 (8 H, m, $ArOCH_2CH_2O$), 4.13-4.23 (10 H, m, $ArOCH_2CH_2$), 6.60 (1 H, s, C-6 CH), 6.94 (1 H, d, J_{ortho} = 8.8 Hz, C-6' CH), 7.41 (1 H, s, C-3 CH), 7.47 (1 H, d, J_{meta} = 2.0 Hz, C-3' CH), 7.55 (1 H, dd, J_{ortho} = 8.8 Hz, J_{meta} = 2.0 Hz, C-5' CH). IR (KBr) 2923 and 2852 (ν CH_2), 1588 and 1509 [ν N=N and/or C=C (aromatic)], 1262 and 1052 (ν COC, aryl ether), 1130 (ν COC, alkyl ether) cm^{-1}. FABMS *m/z* 830 (M^+). *Anal.* Calcd for $C_{46}H_{74}N_2O_{11}$: C, 66.48; H, 8.97; N, 3.37. Found: C, 66.37; H, 8.99; N, 3.31.

Azobis(benzo-15-crown-5) Ionophore (1c). A suspension of hydroxyazobis(benzo-15-crown-5) (**8**; 58 mg, 0.10 mmol), (*RS*)-**9** (75 mg, 0.10 mmol) and K_2CO_3 (0.3 g, 2 mmol) in DMSO (20 mL) was stirred at 80 °C for 6 h. The ocher solid obtained after usual workup was purified by column chromatography [silica gel; $CHCl_3$-MeOH (95:5)] to give analytically pure **1c** as a yellow powder (91 mg, 79%): mp 95-95.5 °C. ^{1}H-NMR ($CDCl_3$) δ 0.88 (6 H, t, J = 6.8 Hz, CH_3), 1.25 [60 H, br s, $CH_3(CH_2)_{15}(CH_2)_2O$], 1.55 (4 H, m, $CH_2CH_2CH_2O$), 3.42-3.47 and 3.58-3.74 [2 H and 6 H, two m, $OCH_2CH(OCH_2R)CH_2OCH_2R$], 3.75-3.81 [16 H, m, $ArO(CH_2)_2O(CH_2)_2O$], 3.85-3.96 (8 H, m, $ArOCH_2CH_2$), 4.15-4.32 (9 H, m, OCH and $ArOCH_2CH_2$), 6.64 (1 H, s, C-6 CH), 6.93 (1 H, d, J_{ortho} = 8.3 Hz, C-6' CH), 7.37 (1 H, s, C-3 CH), 7.46 (1 H, d, J_{meta} = 2.4 Hz, C-3' CH), 7.52 (1 H, dd, J_{ortho} = 8.3 Hz, J_{meta} = 2.4 Hz, C-5' CH). IR (KBr) 2918 and 2850 (ν CH_2), 1589 and 1506 [ν N=N and/or C=C (aromatic)], 1258 and 1055 (ν COC, aryl ether), 1130 (ν COC, alkyl ether) cm^{-1}. FABMS *m/z* 1157 (M^++1). *Anal.* Calcd for $C_{67}H_{116}N_2O_{13}$: C, 69.50; H, 10.11; N, 2.42. Found: C, 69.30; H, 10.27; N, 2.33.

Reference Ionophore (3). A suspension of 4'-(*p*-hydroxyphenylazo)benzo-15-crown-5 (**13**; 0.39 g, 1.0 mmol), triethylene glycol monododecyl ether *p*-toluenesulfonate (**14**; 0.47 g, 1.0 mmol) and K_2CO_3 (0.5 g, 4 mmol) in DMSO (50 mL) was stirred at 80 °C for 6 h. The ocher solid obtained after usual workup was purified by column chromatography [silica gel; CH_2Cl_2-MeOH (95:5)] to give analytically pure **3** as a yellow powder (0.47 g, 68%): mp 94-94.5 °C. ^{1}H-NMR ($CDCl_3$) δ 0.87 (3 H, t, J = 6.8 Hz, CH_3), 1.25 [18 H, br s, $CH_3(CH_2)_9(CH_2)_2O$), 1.57 (2 H, quintet, J = 6.8 Hz, $CH_2CH_2CH_2O$), 3.45 (2 H, t, J = 6.8 Hz, CH_2CH_2O), 3.57-3.61, 3.63-3.68, 3.68-3.72 and 3.73-3.77 [each 2 H, four m, $ArO(CH_2)_2OCH_2CH_2OCH_2CH_2OR$], 3.77-3.80 [8 H, m, $ArO(CH_2)_2O(CH_2)_2$ (crown ring)], 3.88-3.92 and 3.92-3.97 (2 H and 4 H, two m, $ArOCH_2CH_2$), 4.19-4.26 (6 H, m, $ArOCH_2$), 6.96 (1 H, d, J_{ortho} = 8.8 Hz, C-6 CH), 7.01 (2 H, d, J_{ortho} = 8.8 Hz, C-2',6' CH), 7.46 (1 H, d, J_{meta} = 2.0 Hz, C-3 CH), 7.55 (1 H, dd, J_{ortho} = 8.8 Hz, J_{meta} = 2.0 Hz, C-5 CH), 7.85 (2 H, d, J_{ortho} = 8.8 Hz, C-3',5' CH). IR (KBr) 2922 and 2852 (ν CH_2), 1595 and 1504 [ν N=N and/or C=C (aromatic)], 1250 and

1059 (ν COC, aryl ether), 1114 (ν COC, alkyl ether) cm^{-1}. MS *m/z* 688 (M^+). *Anal.* Calcd for $C_{38}H_{60}N_2O_9$: C, 66.24; H, 8.78; N, 4.07. Found: C, 66.05; H, 8.86; N, 4.00.

Preparation of PVC-supported Liquid Membranes. PVC-supported liquid membranes containing ionophores (**1b**), (**1c**) and (**3**) were prepared according to the procedure described previously.[10] The membranes were prepared by mixing DBP (500 mg), PVC powder (250 mg) and ionophore (0.005~0.5 mg), then adding THF (2.5 mL), and finally stirring the suspension until PVC was dissolved completely. The resulting solution was carefully cast onto a flat Petri dish and allowed to stand for 20 h to evaporate THF. The thickness of the PVC membrane thus obtained (*ca.* 10 mm diameter) was approximately 50 μm, as measured by a micrometer.

Absorption Spectra. The ratios of the *trans* and *cis* isomers of the photoswitchable ionophores (**1b**), (**1c**) and (**3**) in the membrane were determined by measuring the absorption spectra using a UV-visible spectrometer (UV-240, Simadzu, Kyoto, Japan). Photoirradiation was made with a 150 W xenon lamp (Ushio Electric, Tokyo, Japan) using cut-off filters Hoya B-420 (< 420 nm) and Toshiba Y-49 (> 490 nm) for obtaining UV and visible lights, respectively. The *cis* percentage of the ionophore in the membrane was estimated from the change in the absorption intensity at the π-π^* absorption maximum of the *trans* azobenzene chromophore (400, 398 and 368 nm for **1b**, **1c** and **3**, respectively). Since the absorption spectra of the *cis* isomers could not be obtained directly, an assumption had to be made that the absorbance of the *cis* isomer at the wavelength used is negligible in comparison to that of the *trans* isomer.[2a,b]

Liquid-liquid Extraction. Aqueous solution (3 mL) containing 5.00×10^{-5} M picric acid, 1.00×10^{-3} M alkali metal hydroxide and 5.00×10^{-1} M alkali metal chloride was vigorously shaken under visible or UV light irradiation with an equal volume of DBP containing 1.00×10^{-3} M photoswitchable ionophore. After sufficient agitation at 25 °C, the concentration of picrate in the aqueous phase was determined from the absorbance at 354 nm within 1 min after the end of irradiation. The change in the concentration of the extracted picrate due to the change in the *cis/trans* ratio during the period from the end of irradiation to the spectroscopic measurement was neglected because the thermal conversion from the *cis* to the *trans* isomer would be sufficiently slow, particularly in water-saturated organic solvent.[2a]

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