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Photocontrolled Binding of Metal Ions with Thioindigo Derivatives Containing Oxyethylene Chains

S. M. Fatah-ur RAHMAN, Koushi FUKUNISHI,* Masaki KUWABARA, Hiroki YAMANAKA, and Mototeru NOMURA
Department of Chemistry and Materials Technology, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606

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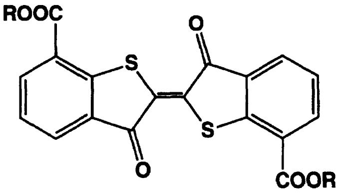
Binding ability of a series of thioindigo derivatives(**Ia—g**), which possess a molecular architecture, capable of capturing different metal ions was examined. From the results of solvent extraction the order of extractibility for metal ions by *cis*-**Ig** was found as $Ag^+ \gg Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. Enhancement of excellent binding ability by trans to cis photoisomerization of **Ig**, the highest amount of transported Ag^+ across a liquid membrane by **Ig** when irradiated with 550 and 480 nm light alternately, and the considerable suppression for thermal cis-to-trans isomerization in presence of Ag^+ were found.

Light is used as trigger for subsequent processes in many photoresponsive systems. Both in animals and plants the photoresponsive systems play remarkable role for survival. Photosynthesis, vision, phototaxis etc. may be cited as typical examples. Several attempts had been successfully made to obtain desired structural change by introducing photoantenna.[1)] Structural changes of many substances occurred when photoinduced,[2)] the results of which are of interest in converting light energy to chemical function. Since the time of Pedersen extensive studies of the nature of the complexes formed by the macrocyclic polyethers and also by acyclic crown ether like macromolecules, mentioned in a number of papers, with many salts have been done by a number of techniques such as, isolation of the solid crystalline complexes,[3)] solubilization of salts in organic solvents,[4)] extraction studies[5)] and proton magnetic resonance studies.[6)] Ion transport through membranes is also a widely accepted and well established phenomenon.[7)] Macrocyclic polyethers, termed as ion bearers, contain intramolecular cavities designed by molecular segments and are capable of specific interaction with alkali and alkaline earth metal ions. Redox- and photocontrolled binding ability of macrocyclic crown ethers have been reported in a number of papers.[1,8)]

Crown ether-like thioindigo derivatives containing oxyethylene chains, were first designed as photoresponsive host molecules by M. Irie et al.[9)] and recently reported by us.[10)] We have extended this idea to the potentially important macromolecular thioindigo dyes possessing two, three, four and five oxyethylene groups which are indispensable for the complexation with metal ions. We were interested in the coordination ability of S-ligands of thioindigo dyes to metal ions, particularly with respect to the role of possible Ag–O and Ag–S interactions, as suggested by the above literature.[9)] The present study is to examine the effect of the variable lengths of oxyethylene chains on metal ion binding and transportation through liquid membrane when the ring shapes formed by these oxyethylene chains reversibly changed in response to a photon captured by the thioindigo chromophore (Scheme 1).



$R = (CH_2CH_2O)_mC_nH_{2n+1}$

Ia; m = 1, n = 1
Ib; m = 1, n =12
Ic; m = 2, n = 1
Id; m = 2, n = 12
Ie; m = 3, n = 1
If; m = 3, n = 12
Ig; m = 4, n = 12
Ih; m = 5, n = 12

Scheme 1.

Experimental

General. All chemicals were reagent grade and used without further purification unless otherwise specified. Melting points were taken on a Yanagimoto micro melting point apparatus and are uncorrected. The UV-vis spectra were recorded on a U-3410 Hitachi spectrophotometer. ^1H NMR spectra were run on a FT NMR QE 300 MHz Shimadzu spectrometer. Mass spectra were taken on a M-80 B Hitachi mass spectrometer. Chromatography was done on a 3 cm×70 cm column of silica gel with a mixed solvent of chloroform and ethyl acetate. 1,2-Dichloroethane used for solvent extraction was spectroanalytical grade.

Synthesis. Dyes **I** were synthesized from 2,2′-dithiodibenzoic acid as described in the literature.[9)] Different lengths of oxyethylene groups which are the constituent units for crown ether-like cavity were introduced at the 7, 7′-positions by ester linkages. The general structure (trans form) of **I** is represented in the Scheme 1.

7,7′-Bis(2-methoxyethoxycarbonyl)thioindigo (Ia):[9)] Yield 6.5%; mp 235—236 °C; ^1H NMR ($CDCl_3$) δ=8.355 (2H, d, aromatic), 8.129 (2H, d, aromatic), 7.436 (2H, t, aromatic), 4.602 (4H, t, $OCOCH_2$), 3.831 (4H, t, $OCOCH_2C\underline{H}_2$), 3.504 (6H, s, OCH_3). Found: *m*/*z* 500.0590. Calcd for $C_{24}H_{20}O_8S_2$: M, 500.0599.

7,7′-Bis[2-(dodecyloxy)ethoxycarbonyl]thioindigo (Ib):[11)] Yield 3.8%; mp 135—137 °C; ^1H NMR ($CDCl_3$) δ=8.346 (2H, d, aromatic), 8.119 (2H, d, aromatic), 7.430 (2H, t, aromatic), 4.591 (4H, t, $OCOCH_2$), 3.853 (4H, t,

$OCOCH_2C\underline{H}_2$), 3.579 (4H, t, $OC\underline{H}_2CH_2$), 1.558 (4H, t, $OCH_2C\underline{H}_2$), 1.224 (36H, s), 0.860 (6H, t, $CH_2C\underline{H}_3$). Found: m/z 808.4033. Calcd for $C_{46}H_{64}O_8S_2$: M, 808.4043.

7, 7′- Bis[[2- (2- methoxyethoxy)ethoxy]carbonyl]-thioindigo (Ic):[11] Yield 5.0%; mp 180—182 °C; ^{1}H NMR ($CDCl_3$) δ=8.334 (2H, d, aromatic), 8.104 (2H, d, aromatic), 7.424 (2H, t, aromatic), 4.608 (4H, t, $OCOCH_2$), 3.937 (4H, t, $OCOCH_2C\underline{H}_2$), 3.790 (4H, t, $OC\underline{H}_2CH_2$), 3.615 (4H, t, $OCH_2C\underline{H}_2$), 3.393 (6H, s, OCH_3). Found: m/z 588.1113. Calcd for $C_{28}H_{28}O_{10}S_2$: M, 588.1124.

7, 7′- Bis[[2- [2- (dodecyloxy)ethoxy]ethoxy]carbonyl]thioindigo (Id):[11] Yield 3.2%; mp 125—126 °C; ^{1}H NMR ($CDCl_3$) δ=8.329 (2H, d, aromatic), 8.102 (2H, d, aromatic), 7.417 (2H, t, aromatic), 4.600 (4H, t, $OCOCH_2$), 3.936 (4H, t, $OCOCH_2C\underline{H}_2$), 3.777 (4H, t, $OC\underline{H}_2CH_2$), 3.638 (4H, t, $OCH_2C\underline{H}_2$), 3.452 (4H, t, $OC\underline{H}_2CH_2$), 1.558 (4H, t, $OCH_2C\underline{H}_2$), 1.224 (36H, s), 0.860 (6H, t, $CH_2C\underline{H}_3$). Found: m/z 896.4542. Calcd for $C_{50}H_{72}O_{10}S_2$: M, 896.4567.

7, 7′- Bis[[2- [2- (2- methoxyethoxy)ethoxy]ethoxy]-carbonyl]thioindigo (Ie):[9] Yield 6.5%; mp 132—133 °C; ^{1}H NMR ($CDCl_3$) δ=8.321 (2H, d, aromatic), 8.096 (2H, d, aromatic), 7.416 (2H, t, aromatic), 4.590 (4H, t, $OCOCH_2$), 3.922 (4H, t, $OCOCH_2C\underline{H}_2$), 3.793 (4H, t, $OC\underline{H}_2CH_2$), 3.710 (4H, t, $OCH_2C\underline{H}_2$), 3.650 (4H, t, $OC\underline{H}_2CH_2$), 3.522 (4H, t, $OCH_2C\underline{H}_2$), 3.345 (6H, s, OCH_3). Found: m/z 676.1648. Calcd for $C_{32}H_{36}O_{12}S_2$: M, 676.1648.

7, 7′- Bis[[2- [2- [2- (dodecyloxy)ethoxy]ethoxy]ethoxy]carbonyl]thioindigo (If):[11] Yield 3.5%; mp 127—129 °C; ^{1}H NMR ($CDCl_3$) δ=8.367 (2H, d, aromatic), 8.137 (2H, d, aromatic), 7.449 (2H, t, aromatic), 4.617 (4H, t, $OCOCH_2$), 3.946 (4H, t, $OCOCH_2C\underline{H}_2$), 3.806 (4H, t, $OC\underline{H}_2CH_2$), 3.734 (4H, t, $OCH_2C\underline{H}_2$), 3.671 (4H, t, $OC\underline{H}_2CH_2$), 3.577 (4H, t, $OCH_2C\underline{H}_2$), 3.436 (4H, t, $OC\underline{H}_2CH_2$), 1.536 (4H, t, $OCH_2C\underline{H}_2$), 1.247 (36H, s), 0.879 (6H, t, $CH_2C\underline{H}_3$). Found: m/z 984.5109. Calcd for $C_{54}H_{80}O_{12}S_2$: M, 984.5091.

7,7′-Bis[[2-[2-[2-[2-(dodecyloxy)ethoxy]ethoxy]ethoxy]ethoxy]carbonyl]thioindigo (Ig):[12] Yield 2.5%; mp 125—126 °C; ^{1}H NMR ($CDCl_3$) δ=8.352 (2H, d, aromatic), 8.124 (2H, d, aromatic), 7.443 (2H, t, aromatic), 4.610 (4H, t, $OCOCH_2$), 3.941 (4H, t, $OCOCH_2C\underline{H}_2$), 3.795 (4H, t, $OC\underline{H}_2CH_2$), 3.733 (4H, t, $OCH_2C\underline{H}_2$), 3.618—3.687 (12H, m), 3.573 (4H, t, $OCH_2C\underline{H}_2$), 3.433 (4H, t, $CH_2C\underline{H}_2$), 1.564 (4H, t, $C\underline{H}_2C_9H_{18}$), 1.246 (36H, s), 0.876 (6H, t, $CH_2C\underline{H}_3$). Found: C, 64.38; H, 8.10%. Calcd for $C_{55}H_{88}O_{14}S_2$: C, 64.90; H, 8.26%.

7, 7′- Bis[[2- [2- [2- [2- [2- (dodecyloxy)ethoxy]ethoxy]ethoxy]ethoxy]ethoxy]carbonyl]thioindigo (Ih): Yield 2.0%; mp 117—118 °C; ^{1}H NMR ($CDCl_3$) δ= 8.353 (2H, d, aromatic), 8.125 (2H, d, aromatic), 7.446 (2H, t, aromatic), 4.609 (2H, t, $OCOCH_2$), 3.939 (4H, t, $OCOCH_2C\underline{H}_2$), 3.798 (4H, t, $OC\underline{H}_2CH_2$), 3.721 (4H, t, $OCH_2C\underline{H}_2$), 3.616—3.681 (20H, m), 3.571 (4H, t, $OCH_2C\underline{H}_2$), 3.436 (4H, t, $OC\underline{H}_2CH_2$), 1.567 (4H, t, $C\underline{H}_2C_9H_{18}$), 1.247 (36H, s), 0.876 (6H, t, $CH_2C\underline{H}_3$).

Method of Solvent Extraction. Prior to solvent extraction and transportation experiments the 1,2-dichloroethane solutions of **I** were photoirradiated with 150 W tungsten–halogen lamp using appropriate filter. The absorption maximum ($\lambda_{\rm max}$) due to trans form was found to be 534 nm and that for cis form was 485 nm when irradiated with 480 and 550 nm light, respectively, as shown in Fig. 1.

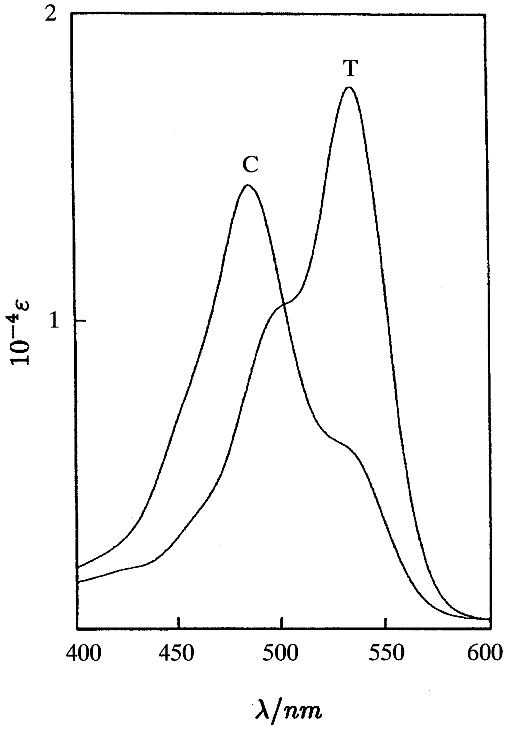


Fig. 1. Absorption spectra of **Ig** in 1,2-dichloroethane. T(trans) and C(cis) are the photostationary state spectra under irradiation with 480 and 550 nm light, respectively.

Solvent extraction was done in a 20 ml single test tube taking equal volumes (4 ml) of organic solution (1,2-dichloroethane) containing 0.04 mmol dm^{-3}of **I** and an aqueous solution containing 20 mmol dm^{-3} of metal nitrate and 0.02 mmol dm^{-3} of picric acid. The organic layer of the test tube was irradiated with 550 nm light for one minute and then vigorously agitated for two hours by a vertical shaker. The extractibility was then determined from the differences of the absorbances of the picrate in the aqueous phase (before irradiation and after agitation). The extraction experiments were conducted at 25 °C and in all cases the test tubes were protected from light during shaking to avoid photoisomerization. Similarly, blank experiments were performed with pure organic solvent containing nothing as host molecules.

Method of Ion Transport across a Liquid Membrane. Transport of metal ions across a liquid membrane of 1,2-dichloroethane (15 ml) containing **I** (0.04 mmol dm^{-3}) as a carrier was examined by the H-type cell using the procedure adopted by Irie et al.[9] Two aqueous phases separated by an organic membrane were taken in the H-type cell. Aqueous phase A (6 ml) contained a mixture of metal nitrate (20 mmol dm^{-3}) and picric acid (0.02 mmol dm^{-3}) and phase B (6 ml) contained pure water. The organic phase was irradiated for one minute with 550 nm light and then stirred gently. After two hours the stirring was ceased and the orgnic phase below the aqueous phase B was irradiated with 480 nm light for 30 s. In this way the metal ions were transported from the aqueous phase A to phase B. The decrease of the absorbance of the aqueous phase A and the increase of the absorbance of the aqueous phase B were followed by spectroscopically.

Results and Discussion

The configurational change of **I** which expectedly occurred with trans–cis isomerization, was effectively used in solvent extraction and transportation of metal ions through organic membrane. Configurational changes from trans-to-cis and cis-to-trans forms of **I** were done by the irradiation with 550 and 480 nm light, respectively. Figure 1 shows the absorption spectra of **Ig** where T and C stand for trans and cis forms having absorption maxima at 534 and 485 nm, respectively. Absorption spectra of all the other derivatives used in this experiment were similar to that of **Ig**.

Photocontrolled Solvent Extraction. The combination of an aqueous phase containing picrate and an organic phase containing **I** was used in the extraction experiment because the absorption maximum of the picrate (355 nm) did not overlap with that of **I**. The extraction method adopted in this experiment was a convenient way of comparing relative complexing powers of the dyes of **I** series for different cations. The intensity of complexing powers can be quantitatively determined from the difference of the picrate absorption band. In the blank experiments of two immiscible solvents no transference of the picrate occurred but using the organic solvent containing **I** the complexed picrate transferred to the organic solvent. According to the complexing powers of the different thioindigo derivatives the absorbances of the picrate decreased after extraction compared to the initial absorbance.

Figure 2 shows the change of absorbance of the picrate i.e., the Ag^+ extraction into the organic phase and the ion release back to the aqueous phase regulated by alternate photoirradiation in a single test tube. Obtaining a photo signal at 550 nm for one minute the photogenerated *cis*-**Ig** extracted about 18% (estimated from the decrease of the absorption of the picrate in the aqueous phase) of Ag^+ into the organic phase in two hours, as shown by the open circles in the downward direction in Fig. 2. After two hours of extraction the test tube was kept in dark on constant stirring and it was found that negligible amount of Ag^+ released back to the aqueous phase, shown also by the open circles in the horizontal direction, in 24 h because of extremely slow thermal isomerization. But on irradiation with 480 nm light for 30 s the captured Ag^+ was released back to the aqueous phase shown by the filled circles, the final concentration of which was reached 8% lower than the initial one. Retention of the above mentioned Ag^+ in the organic phase was due to the *cis*-**Ig** which remained unisomerized when irradiated with 480 nm light and also due to the trans form of **Ig**, capable of capturing reasonable amount of Ag^+, shown in the Table 1. Extraction experiments with the alkali metal ions and also with silver ion were conducted. The results of the extraction of the picrates with **Ig** are summarized in Table 1. Examination of the Table 1 revealed the following: (i) the order of extractibility by *cis*-**Ig** was $Ag^+ \gg Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, (ii) extractibility of *cis*-**Ig** was greater for the alkali metal ions having larger ionic diameter, (iii) extractibility can be increased by photoisomerization from trans to cis form. These results might be explained in terms of photoinduced suitable forms that is, cis forms, for metal ion binding. A graphical representation of the extractibility of dyes **I** for Ag^+ is shown in Fig. 3. The results of the extraction revealed that **Ig** and **Ih** of the **I** series were the excellent complexing agents for Ag^+ and in general, the most effective for the other cations. It can also be said that **Ig** has excellent selectivity towards Ag^+. Extraction of Ag^+ is always found to be better by the cis isomers compared to the trans isomers of the dyes studied except **Ih**. Especially there is a distinct promotion for *cis*-**Ig** showing about four times selectivity than that of *trans*-**Ig**. Additionally, elongation of oxyethylene chain from one to four gave a nine fold increase in extractibility suggesting that electrostatic interaction between Ag^+ and oxygen atoms[13] and additional force between soft Ag^+ and soft sulfur

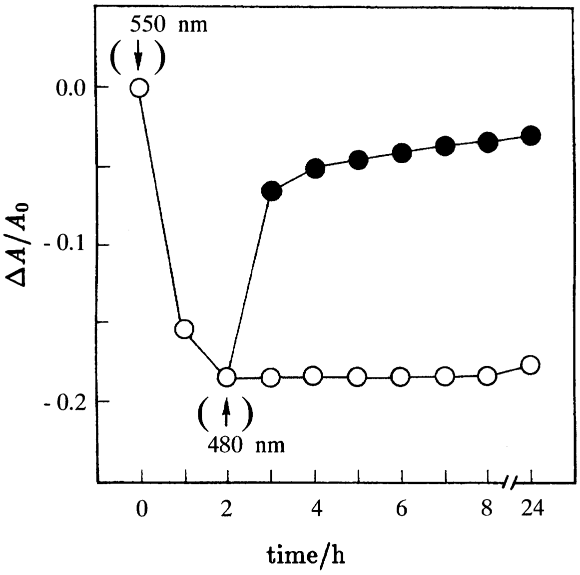


Fig. 2. Photoregulated capture and release of Ag^+ by **Ig** in a single test tube. Change of absorbance of silver picrate: ○, on irradiation of the organic phase with 550 nm light for 1 min; ●, on irradiation with 480 nm light for 30 s.

Table 1. Extraction of Metal Ions by **Ig**[a)]

	Metal picrate extracted/%					
Carrier	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+
trans-**Ig**	1.0	1.2	1.0	1.0	0.9	4.8
cis-**Ig**	0.8	1.7	3.1	3.6	4.1	18.4

a) Organic phase, 1,2-dichloroethane solution containing **Ig** (0.04 mmol dm^{-3}); aqueous phase, aqueous solution containing a mixture of metal nitrate (20 mmol dm^{-3}) and picric acid (0.02 mmol dm^{-3}).

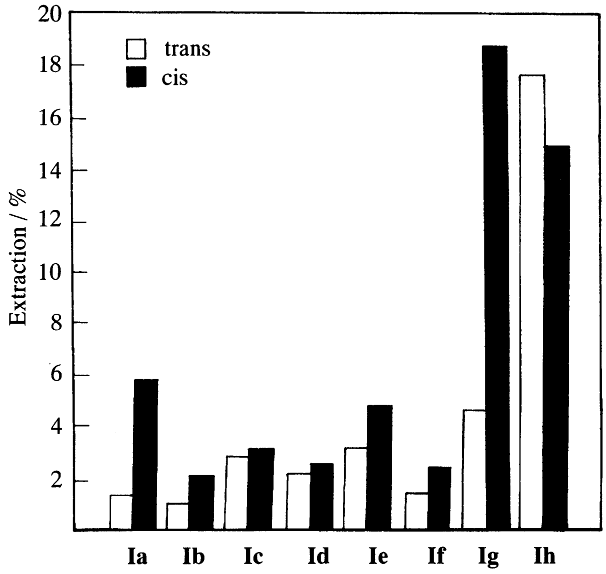


Fig. 3. Extraction of Ag^+ with **I**.

atoms[14)] may exist in their conformation. The tops of the bars depicting maximum extractibility of the cis isomers in Fig. 3 when connected exhibit the saw-toothed pattern depending on the alkyl groups, methyl and dodecyl, at the terminals. This might be understood from the extractibility that decreased because of the crowding nature of the long alkyl chain when the dyes form complexes with Ag^+. Thus thioindigo dyes having four or five oxyethylene units and a terminal of only methyl group, which could more effectively bind Ag^+, would be expected. Unfortunately, our attempt to synthesize the above mentioned dye was unsuccessful. We also conducted experiments with the thioindigo derivatives[11)] having alkyl chains with no oxyethylene units and did not find any extraction of metal ions. This result indicates that without the oxyethylene chains it is not possible to make a cavity to hold the metal ions. In other words it can be said that oxygen atoms are indispensable for metal ion binding, though it is not sufficient to obtain the effective transport of Ag^+ by using only long oxyethylene chains. Crown ethers having sulfur atoms in the ring[15)] and in the side arm[16)] are known to show high and specific binding to Ag^+. X-ray analysis for the complexation of Ag^+ by mixed S–O crowns confirms that transport of Ag^+ may occur via Ag···O interaction as well as Ag–S bonding, suggesting the 1 : 1, 2 : 1, and 3 : 2 complex formation.[17)] Therefore, such high selectivity of **Ig** for Ag^+ may be caused by cooperative interaction of sulfur atoms and oxygen atoms accommodated in the relevent conformation, despite the presence of disorder in the macrocyclic-like ring.

Interestingly, it is also seen that the extraction of Ag^+ with **Ih** shows a different trend. Unlike **Ig** the extractibilities of both *trans-* and *cis*-**Ih** were considerably high. The reason for high extraction of the trans form might be attributed to the capability of the single chain with five oxyethylene units which is supposed to form independent cavity on both sides of the rigid thioindigo chromophore.

Ion Transport across a Liquid Membrane. Transportation of metal ions through the liquid membrane utilizing physical or chemical phenomena have been reported.[18)] In this work light has been used as a convenient source to control the rate of ion transport. Transport experiments of different metal ions were done within an H-type cell. Metal ions were transported from phase A to phase B by alternate irradiation of the organic phase beneath the aqueous phase A and phase B. In the dark no transference of ion occurred from the phase A to the phase B. Repeating four times the alternate photoirradiation with 550 and 480 nm light transportation of Ag^+ with different thioindigo dyes was effectively performed. Absorption spectrum of the B phase coincides in its pattern with that of the picrate in the A phase and ca. 90% of the picrate reduced from the source phase was recovered in the phase B. In the Table 2 it is shown that the maximum amount of Ag^+ was transported with the aid of **Ig** repeating the capture and release cycle for four times. It was observed in this experiment that the rate of transportation was increased by 2.4 to 3.5 fold for **Ig**. This trend was also in line with the extraction% shown in Fig. 3.

Influence of Ag^+ on the Rate of Configurational Change. The configurational changes of the thioindigo derivatives can also be brought about by cis to trans thermal isomerization because of lack of thermodynamic stability of cis form. The regeneration of trans form from cis form in the dark can be followed by spectrophotometrically. In this experiment the increase in the absorption band of *trans*-**I** (λ_{max} 534 nm) was monitored as a function of time at 50 °C. The isosbestic points at 337 and 497 nm were maintained both in the presence and in the absence of silver ion suggesting no side reaction during thermal isomerization. The logarithms of absorbance plotted against time satisfied a first-order equation. The values of the first-order rate constants (k) found for the transformation of cis isomers of **I** to the corresponding trans isomers are shown in Table 3.

Table 2. Photoregulated Transport of Ag^+ across a Liquid Membrane[a)]

Carrier	Transported Ag^+/% 1st	2nd	3rd	4th
Ia	6.0	10.6	12.0	14.0
Ie	7.0	9.6	12.6	17.0
If	5.4	7.6	9.0	11.7
Ig	18.4	24.2	31.2	40.5

a) Ag^+ transported from phase A to phase B in the H-type cell by repeating alternate irradiation cycle (each cycle 4 h) for four times.

Table 3. Influence of Ag^+ on the Rate of Cis-to-Trans Configurational change of **Ia**, **Ig**, and **Ih** at 50 °C

	$k\times10^5/s^{-1}$	
	In absence of Ag^+	In presence of Ag^+
Ia	3.60	0.63
Ig	0.43	0.19
Ih	1.21	0.18

From these results it is understood that the rate of configurational change from cis to trans form is considerably suppressed in the presence of Ag^+. The reason for the suppression may be ascribable to the interaction of oxygen atoms, deployed by their periodic insertion within the cavity and also of sulfur atoms, with Ag^+.

The present work demonstrated efficient binding of Ag^+ and transportation through a liquid membrane containing thioindigo dyes (**I**) modified with different lengths of oxyethylene chains which was fully controlled by light. Especially **Ig** with four oxyethylene units can transport Ag^+ with excellent selectivity and high efficiency through liquid membrane.

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