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ENHANCED PHOTOCONTROLLED BINDING OF AG$^+$ BY THIOINDIGO DERIVATIVE CONTAINING OXYETHYLENE CHAINS WITH OH GROUPS AT THE TERMINAL POSITIONS

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ABSTRACT

A novel thioindigo dye was synthesized, from 7, 7'-bis-chlorocarbonyl thioindigo, containing OH groups at the terminal positions of the oxyethylene side chains. The resultant dye 7, 7'-Bis[[2-[2-(2-hydroxyethoxy)ethoxy]ethoxycarbonyl]thioindigo (1) was characterized by ^{1}H NMR, IR, and mass spectral studies. The thioindigo derivative (1), which possesses a molecular architecture, undergoes reversible photochromic reaction and capable of capturing different metal ions and transports them through liquid membrane. Enhancement of binding ability (i) by incorporating OH groups instead of large phenyl or methyl groups, (ii) by trans to cis photoisomerization of (1), iii) the highest amount of transported Ag$^+$ by (1) across a liquid membrane when irradiated with 550 and 480 nm light alternately, were found.

Key words: Solvent extraction, Photo responsive, Thioindigo derivative

INTRODUCTION

Although the indigoid dyes have been used traditionally as colouring matters for textiles and other substrates for thousands of years, today the focus of research on indigoid dye chemistry is changing. Macro cyclic polyethers have been extensively studied since Pedersen, (Pedersen 1970 a, b) but photo control had not been achieved before 80‘s on host molecules containing the crown ether. Several attempts had been successfully made to obtain desired structural change by introducing photo antenna. Much effort has also focused on the photo responsive thioindigo derivatives containing variable lengths of oxyethylene open chains, (Irie and Kato 1985, Fatah-ur-Rahman *et al*. 1993) and thioindigo crown ethers, (Fatah-ur-Rahman and Fukunishi 1994).

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When photoinduced, Fatah-ur-Rahman and Fukunishi (1992), Shinkai *et al.* (1980, 1981), noted that structural changes of many substances occurred, 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 macro-cyclic polyethers and also by acyclic crown ether-like macromolecules, mentioned in a number of papers, with many salts have been done in a number of techniques such as, isolation of the solid crystalline complexes (Pedersen 1967, 1967, 1970 a, b), solubilization of salts in organic solvents (Hiratani *et al.* 1980), extraction studies (Pedersen 1970) and proton magnetic resonance studies (Prestegard and Sunny 1969). Ion transport through membranes is also a widely accepted and well-established phenomenon (Choy *et al*. 1974, Hiratani 1981).

Crown ether-like thioindigo derivatives containing oxyethylene chains, were first designed as photo responsive host molecules by Irie and Kato (1985) and a few years later by the present author, Fatah-ur-Rahman *et al.* (1993). The workers 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 Irie and Kato (1985).

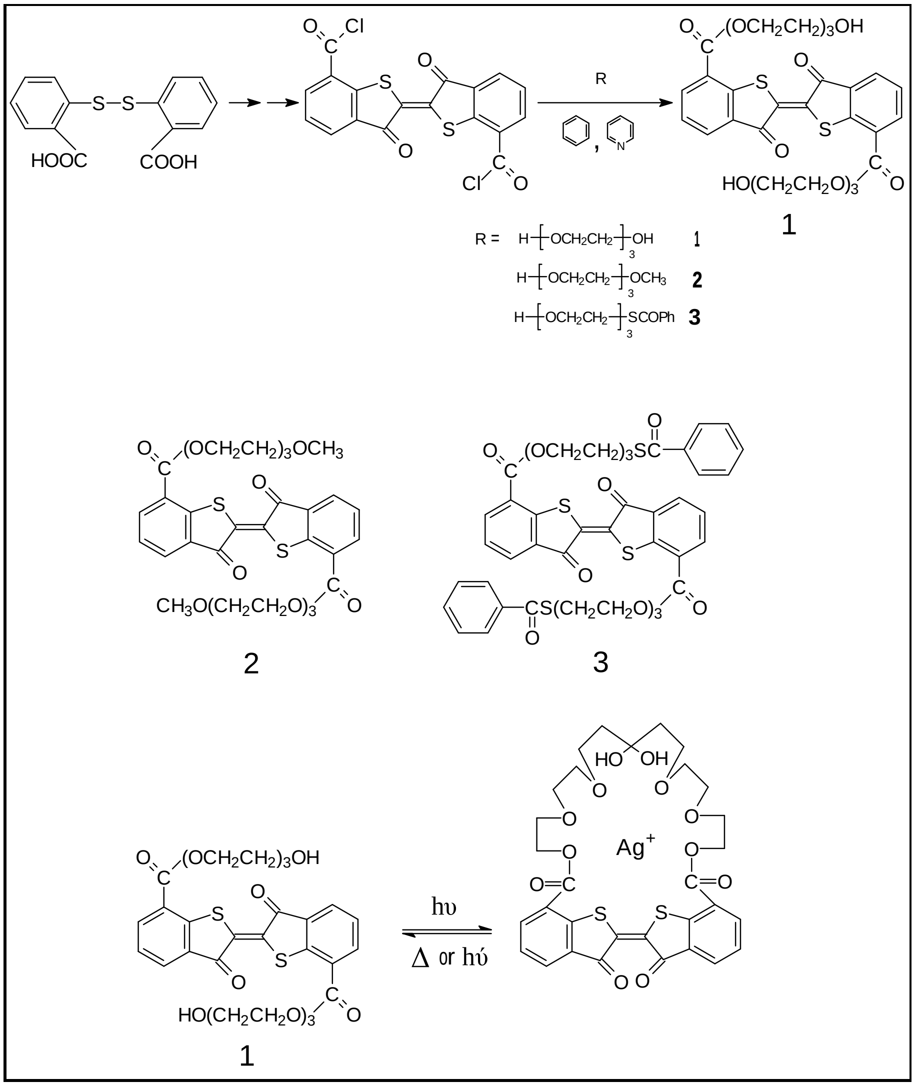
The present study is to examine the effect of similar lengths of oxyethylene chains but different groups at the terminal positions of the chains on metal ions and transportation through liquid membrane when the ring shapes formed by these oxyethylene chains reversibly changed in response to a photon captured by the thioindigo chromophores. The configurational change of 1 which occurred with trans/cis isomerization is used in solvent extraction and the transportation of metal ions through organic membranes. Cooperative ligation with 1 and heavy metals were found.

MATERIALS AND METHODS

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

Synthesis: Synthesis of a new thioindigo derivative 1, as shown in Scheme-1 is reported. Starting from dithiodisalicylic acid, 7, 7’-bis-chlorocarbonyl thioindigo was prepared according to the literature (Irie and Kato 1985). The final product was identified by IR, NMR, UV-VIS and mass spectroscopy.

Scheme 1



HOOC
COOH
S–S
O=C–Cl
R
O=C–(OCH2CH2)3OH
HO(CH2CH2O)3
1
R = H–[OCH2CH2–]3OH 1
H–[OCH2CH2–]3OCH3 2
H–[OCH2CH2–]3SCOPh 3
(OCH2CH2)3OCH3
CH3O(CH2CH2O)3
2
(OCH2CH2)3SC
CS(CH2CH2O)3
3
(OCH2CH2)3OH
HO(CH2CH2O)3
1
hυ
Δ or hύ
HO OH
Ag+

Table 1. Spectral data of 7, 7'-Bis [[2-[2-(2-hydroxyethoxy) ethoxy]ethoxy carbonyl] thioindigo (1), 7, 7'-Bis [[2-[2-(2-methoxyethoxy) ethoxy]ethoxy carbonyl] thioindigo (2) and 7,7'-Bis [[2-[2-(2-benzoylthio ethoxy) ethoxy] ethoxy carbonyl] thioindigo (3) with assignments.

Dye	^{1}H NMR /ppm		Mass (m/z)
Dye 1	8.371	(2H, d, aromatic)	Found : m/z 648.71; Calcd. for $C_{30}H_{32}O_{12}S_2$: M, 648.377
	8.134	(2H, d, aromatic)	
	7.425	(2H, t, aromatic)	
	4.628	(4H, t, $OCOCH_2$)	
	3.956	(4H, t, $OCOCH_2C\underline{H}_2$)	
	3.842	(4H, t, $OCH_2CH_2OC\underline{H}_2$)	
	3.833-3.729	(8H, m)	
	3.631	(4H, t, $OCH_2C\underline{H}_2OH$)	
	2.494	(2H, s, -OH)	
Dye 2 (Fatah-ur-Rahman *et al.* 1993)	8.321	(2H, d, aromatic)	Found : m/z 676.1648; Calcd. for $C_{32}H_{36}O_{12}S_2$: M, 676.1648
	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)	
Dye 3 (Fatah-ur-Rahman and Fukunishi 1992)	8.345	(2H, d, aromatic)	Found : m/z 888.1393; Calcd. for $C_{44}H_{40}O_{12}S_4$: M, 888.1403
	8.101	(2H, d, aromatic)	
	7.912	(4H, d, aromatic)	
	7.541	(2H, t, aromatic)	
	7.411	(6H, t, aromatic)	
	4.611	(4H, t, $OCOCH_2$)	
	3.952	(4H, t, $OCOCH_2C\underline{H}_2$)	
	3.810	(4H, t, $OCH_2CH_2OC\underline{H}_2$)	
	3.761-3.700	(8H, m)	
	3.275	(4H, t, $SC\underline{H}_2$)	

Solvent extraction: Prior to solvent extraction the 1, 2-dichloroethane solution of 1 was photo irradiated with 150W tungsten-halogen lamp using appropriate filter. The absorption maximum (λ_{max}) due to *trans* form was found to be 529 nm and that for *cis* was 483 nm when irradiated with 480 and 550 nm light, respectively, as shown in Fig. 1.

Solvent extraction was done in a single test tube taking equal volumes (4 ml) of organic solution (1,2-dichloroethane) containing 0.04 mmol dm^{-3} of 1, 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 extractability was then determined from the differences of the absorbances of the picrate in the aqueous phase (before irradiation and after irradiation). 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.

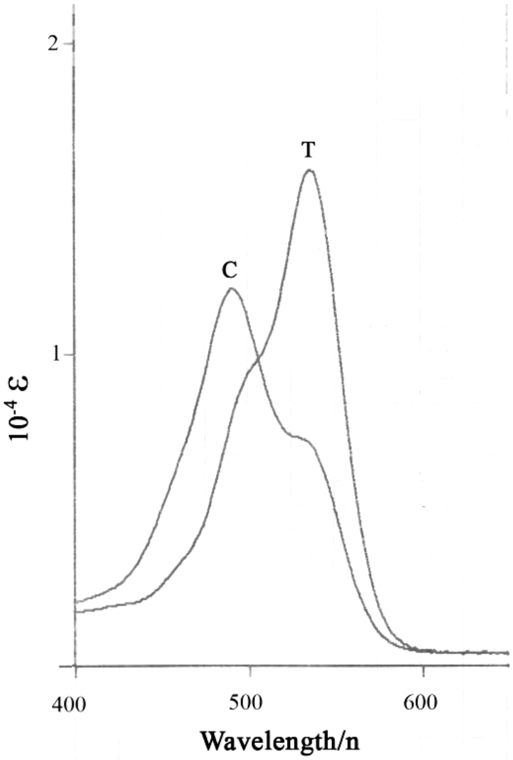


Fig. 1. Absorption spectra of **1** in 1,2-dichloroethane. T (trans) and C (cis) are the photo stationary state spectra under irradiation with 480 and 550 nm light, respectively.

Ion transport across a liquid membrane: Transport of metal ion across a liquid membrane of 1, 2-dichloroethane (15 ml) containing 1 (0.04 mmol dm^{-3} as a carrier was examined by a H-type cell using the procedure adopted by Irie and Kato (1985). Two aqueous phases separated by an organic membrane were taken in the H-type cell. Aqueous phase L (6 ml) contained a mixture of metal nitrate (20 mmol dm^{-3}) and picric acid (0.02 mmol dm^{-3}) and phase R (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 organic phase below the aqueous phase R was irradiated with 480 nm light for 30s.

In this way the metal ions were transported from the aqueous phase L to aqueous phase R. The decrease of the absorbance of the aqueous phase L and the increase of the absorbance of the aqueous phase R were followed by spectroscopically.

RESULTS AND DISCUSSION

Expected configurational change of 1 with *trans-cis* isomerization, was effectively used in solvent extraction and transportation of metal ions through organic membranes. Absorption spectra of other derivatives used in this experiment were similar to that of 1.

Photocontrolled solvent extraction: Picrate in combination with an organic phase containing 1 was used in the extraction experiment because the absorption maximum of the picrate (355 nm) did not overlap with that of 1. The extraction method adopted in this experiment was a convenient way of comparing relative complexing powers of the dyes 1, 2 and 3 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 solvents containing dyes 1, 2 and 3 the complexed picrate transferred to the organic solvents. Ag^+ extraction into the organic phase and the ion release back to the aqueous phase regulated by alternate photoirradiation in a single test tube were examined.

Obtaining a photo signal at 550 nm for one minute the photogenerated *cis*-1 extracted about 21% (estimated from the decrease of the absorption of the picrate in the aqueous phase) of Ag^+ into the organic phase in two hours. 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 in 24 h because of extremely slow thermal isomerization. But on irradiation with 480 nm light for 30s the captured Ag^+ was released back to the aqueous phase, the final concentration of which was reached 6% lower than the initial one. Retention of the above mentioned Ag^+ in the organic phase was due to the *cis*-1 which remained unisomerized when irradiated with 480 nm light. Extraction of the picrates with the alkali metal ions and also with silver ion was conducted.

A graphical representation of the extractability of dye 1 for metal ions is shown in Fig 2.

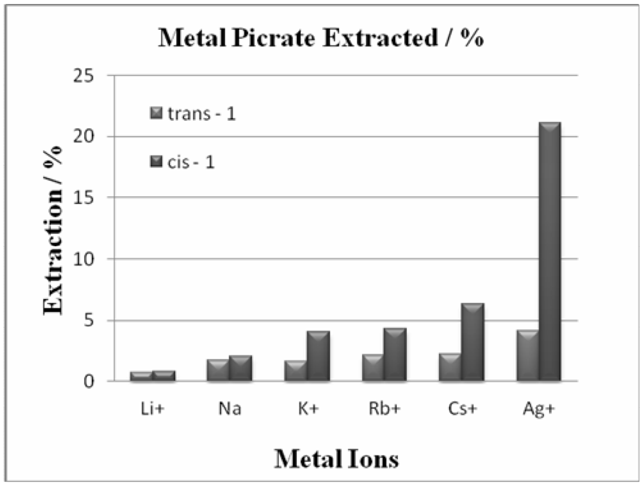


Fig. 2. Extraction of metal Ions with 1 [a)]: (a) Organic phase: 1, 2-dichloroethane solution containing 1 (0.04 mmol dm^{-3}); aqueous phase: aqueous solution containing a mixture of metal nitrate (20 mmol dm^{-3}) and picric acid (0.02 mmol dm^{-3}).

Examination of the Fig. 2 revealed the following: (i) Extractability can be increased by the photoisomerization from *trans* to *cis* form, (ii) the order of extractability by *cis*-1 was $Ag^+ \gg Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$, (iii) extractability of *cis*-1 was greater for the alkali metal ions having larger ionic diameter. These results might be explained in terms of photoinduced suitable forms that is *cis* forms, for metal ion binding.

A graphical representation of the extractability of dyes **1**, **2** and **3** for Ag^+ is shown in **Fig 3.**

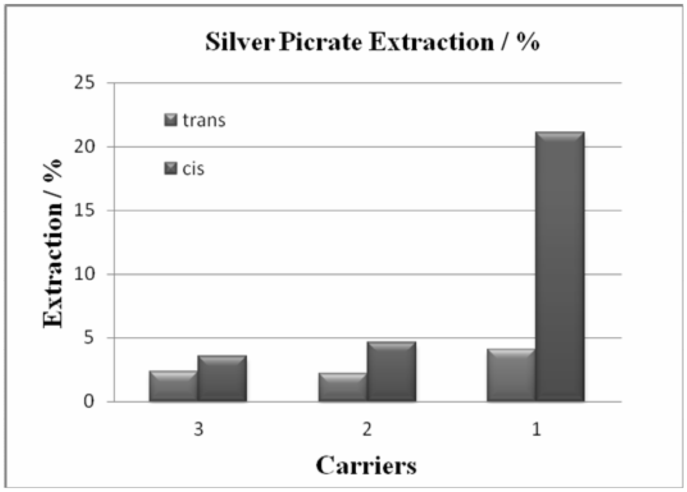


Fig. 3. Extraction of Ag^+ with Dyes[a)] 1, 2 and 3: (a) Organic phase: 1,2-dichloroethane solution containing 1 (0.04 mmol dm^{-3}); aqueous phase: aqueous solution containing a mixture of silver nitrate (20 mmol dm^{-3}) and picric acid (0.02 mmol dm^{-3}).

From the results it can be said that dye 1 is the excellent complexing agent for Ag^+ and in general, the most effective for the other cations. It is clear that there is a distinct promotion for *cis*-1 showing about five times selectivity than that of *trans*-1. Addition of OH group at the terminals of oxyethylene chains gave a six fold increase in extractability suggesting that electrostatic interaction between Ag^+ and oxygen atoms (Kobuke *et al.* 1976, Izatt *et al.* 1971) and additional force between soft Ag^+ and soft sulfur atoms (Broer and Stephen 1990), may exist in their conformation.

Crown ethers having sulfur atoms in the ring (Oue *et al.* 1989, 1988), and in the side arm (Nabeshima *et al.* 1992), 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 formations (Blake *et al.* 1992).

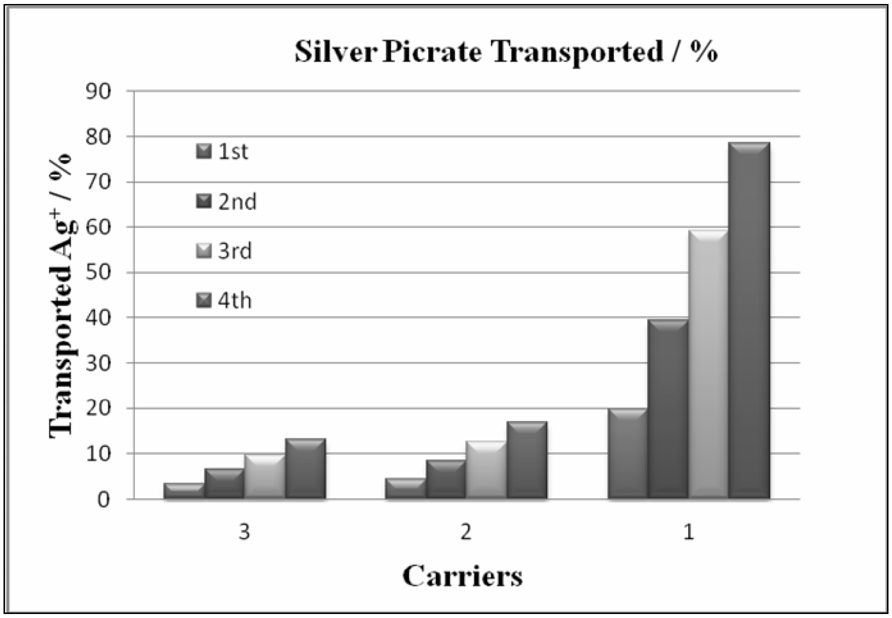


Fig. 4. Photo-regulated Transport of Ag^+ across a Liquid Membrane $^{a)}$: a) Ag+ transported from phase L to phase R in the H-type cell by repeating alternate irradiation cycle (each cycle of 4h) for four times.

Therefore, such high selectivity of 1 for Ag^+ may be caused by cooperative interaction of sulfur and oxygen atoms accommodated in the relevant conformation in the macro cyclic-like ring.

Transportation of metal ions across a liquid membrane: In this work light has been used as a convenient source to control the rate of ion transport. Transportation experiments of different metal ions were done within an H-type cell. Metal ions were transported from phase L to phase R by alternate irradiation of the organic phase beneath the aqueous phase L and phase R. Repeating four times the alternate photoirradiation with 550 and 480 nm light transportation of Ag^+ with thioindigo dyes 1, 2 and 3 was effectively performed. Absorption spectrum of the phase R coincides in its pattern with that of the picrate in the phase L and in this way, ca. 90% of the picrate reduced from the source phase was recovered in the phase R. In the Fig. 4 it is shown that the maximum amount of Ag^+ was transported with the aid of 1 repeating the capture and release cycle for four times. It was observed in this experiment that the rate of transportation was increased by 4.6 to 6 fold for 1. This trend was also in line with the extraction% shown in Fig. 3.

Influence of AG$^+$ on the rate of configurational change: Cis to trans thermal isomerization of thioindigo derivatives in the dark can be followed by spectrophotometrically. Absorption band of trans-1 (λ_{max} 529nm) was monitored as a function of time at 50°C. The isosbestic points at 535 & 505 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 **1** to the corresponding trans isomers are shown in the Table 2.

Table 2. Influence of Ag^+ on the rate of cis to trans configurational change of 1, 2, and 3 at 50°C

	$k \times 10^5 / s^{-1}$	
Carrier	In absence of Ag^+	In presence of Ag^+
3	2.80	0.53
2	1.24	0.19
1	0.79	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 dye 1, 2 and 3 modified with different terminal groups of oxyethylene chains which was fully controlled by light. Dye 1 with OH at the terminal positions of the oxyethylene chains can transport Ag^+ with excellent selectivity and high efficiency through liquid membrane.

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