

## Light-driven Ion-transport mediated by a Photo-responsive Bis(crown ether)

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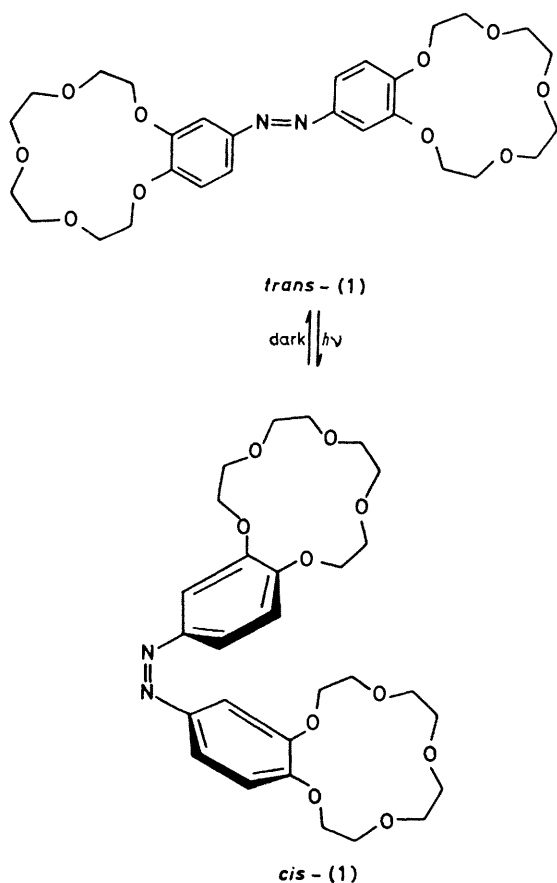
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**Summary** The photo-responsive bis(crown ether) (**1**) acts as a mediator for (i) photo-controlled, selective ion-extraction and (ii) acceleration and deceleration of ion-transport rates by light.

CATIONS are known to be transported through lipid membranes with the aid of synthetic macrocyclic polyethers as well as by antibiotics. Model studies with liquid membrane systems<sup>1</sup> have established that the best carrier for the ion-

transport is a ligand that gives a moderately stable rather than a very stable complex. A very stable complex which may enhance the ion concentration in the transport medium cannot release the ion efficiently from the complex. It occurred to us that, if the binding ability of the ion-carrier can be reduced at the ion-release site (or enhanced at the ion-complexation site) selectively, it could result in an efficient ion-transport system.<sup>2</sup>

Crown ethers form 1:2 cation-crown complexes when the ion radius is greater than the size of the crown ethers (*e.g.*, benzo-15-crown-5 and K<sup>+</sup>).<sup>3</sup> This is reflected by binding abilities: bis(crown ethers) which are able to form intramolecular 1:2 complexes frequently exhibit a binding ability greater than that of the corresponding mono(crown ethers).<sup>4</sup> We thus synthesised the bis(crown ether) (**1**) which changes its structure reversibly, in a 'butterfly' motion, in response to photo-irradiation. We expected that the photo-isomerised *cis*-(**1**) would extract K<sup>+</sup> efficiently from an 'in' aqueous phase into the liquid membrane and the regenerated *trans*-(**1**) would release it rapidly to an 'out' aqueous phase.



The bis(crown ether) (**1**) [*trans*-(**1**)] was prepared from 4'-nitrobenzo-15-crown-5 by zinc powder reduction in the presence of KOH.<sup>†</sup> Photo-isomerisation of *trans*- to *cis*-(**1**) was performed in *o*-dichlorobenzene with a high-pressure Hg-lamp. The ratio of *cis*- to *trans*-(**1**) at equilibrium under these photo-irradiation conditions was 51.4:48.6.<sup>‡</sup> Regeneration of *trans*-(**1**) in the dark was relatively fast (at 30 °C,  $t_{1/2}$  10.3 min in dry *o*-dichlorobenzene and 75.5 min in water-saturated *o*-dichlorobenzene),<sup>§</sup> with eventual quantitative renewal of the initial spectrum of *trans*-(**1**). Preliminary studies of the solvent extraction of alkali metal salts of Methyl Orange from water to *o*-dichlorobenzene<sup>§</sup> established that *trans*-(**1**) extracts Na<sup>+</sup> ion 5.6 times more efficiently than *cis*-(**1**), whereas *cis*-(**1**) extracts K<sup>+</sup> ion 42.5 times more efficiently than *trans*-(**1**). The selectivity, which may be expressed by the ratio [*trans*-(**1**)/*cis*-(**1**)] of extracting ability for Na<sup>+</sup> ion against that for K<sup>+</sup> ion is 238 fold. We believe that this unusually large selectivity stems from the enhanced affinity of *cis*-(**1**) for K<sup>+</sup> ion due to the formation of an intramolecular 1:2 (sandwich-type) complex, because the radius of the K<sup>+</sup> ion is somewhat greater than the size of the 15-crown-5 family.<sup>3,5</sup>

The transport velocity of K<sup>+</sup> ion was measured in a U-shaped glass tube. Potassium picrate was transported at 30 °C with the aid of (**1**) from an 'in' to an 'out' aqueous phase through a bulk liquid *o*-dichlorobenzene membrane. The *o*-dichlorobenzene phase was stirred slowly with a magnetic stirrer. The transport rates which were monitored by following the increase in the absorption intensity of the picrate in the 'out' aqueous phase are summarised in the Table. When the *o*-dichlorobenzene phase was photo-irradiated, the transport velocity was suppressed somewhat, indicating that photo-irradiation may enhance the ion concentration in the *o*-dichlorobenzene phase but does not accelerate the transport velocity. In contrast, when the *o*-dichlorobenzene phase in contact with the 'in' aqueous phase was partially photo-irradiated, the velocity was appreciably increased (see Table and footnotes), suggesting

TABLE. Influence of photo-irradiation on the rates of K<sup>+</sup>-transport through a liquid (*o*-dichlorobenzene) membrane with the aid of (**1**).<sup>a</sup>

Conditions	Initial velocity/ $\mu\text{mol h}^{-1}$
Dark	0.476
Photo-irradiated <sup>b</sup>	0.255
Photo-irradiated <sup>c</sup>	0.735

<sup>a</sup> At 30°C; *o*-dichlorobenzene phase: [(**1**)] =  $2.00 \times 10^{-4}$  M; 'in' aqueous phase: [picric acid] =  $4.00 \times 10^{-3}$  M, [KOH] =  $6.00 \times 10^{-3}$  M, [KCl] = 0.01 M. <sup>b</sup> The *o*-dichlorobenzene phase in the U-tube was irradiated with a high-pressure Hg-lamp for 5 min at intervals of 30 min. <sup>c</sup> The *o*-dichlorobenzene phase in contact with the 'in' aqueous phase was photo-irradiated with a high-pressure Hg-lamp for 5 min at intervals of 30 min. The volume of solution which was photo-irradiated was about one fifth of the total volume of the *o*-dichlorobenzene solution.

<sup>†</sup> M.p. 187–188 °C (yellow needles). The structure was confirmed by its i.r. and mass spectrum, and elemental analysis.

<sup>‡</sup> The composition of the *cis*-(**1**)/*trans*-(**1**) mixture under photo-irradiation conditions and the regeneration rate of *trans*-(**2**) in the dark were affected by added alkali metal cations. The detailed results will be reported in a full paper.

<sup>§</sup> The extraction was carried out at 30 °C. Equal volumes of an *o*-dichlorobenzene solution of (**1**) ( $3.00 \times 10^{-4}$  M) and an aqueous solution of MOH (0.01 M) and Methyl Orange ( $8.10 \times 10^{-6}$  M) were agitated thoroughly for 2 min. The extraction ability was determined by the decrease in the intensity of the absorption band of Methyl Orange in the aqueous solution.

that, if the binding ability of ionophores at the ion-complexation site is selectively enhanced, this leads to an increase in the ion-transport velocity.

In conclusion, the present study demonstrates that the ion-transport velocity through liquid membranes can be controlled, in principle, by switching the light source on and off. Although the rate differences observed in the present experiment are small, we believe that the magnitude of the

response could be amplified by improving the apparatus and the membrane system.

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