# Metal Ion Binding by Photoresponsive Thioindigo Crown Ethers

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Thioindigo crown ethers, containing a disulfide bridge in the side chains, undergo reversible photochromic reaction and bind metal ions and transport them through liquid membranes.

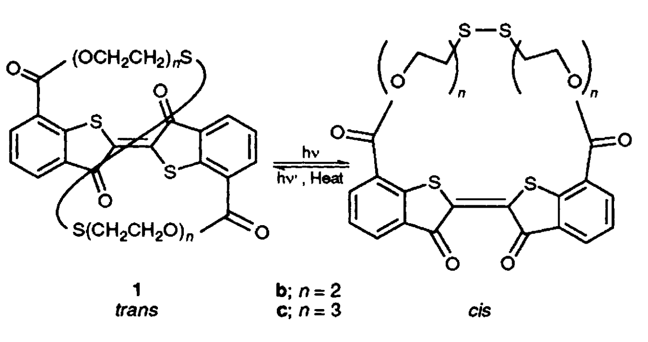
Photocontrol of host molecules has opened a new field of chemistry. Macrocyclic polyethers have been extensively studied since Pedersen, but photocontrol had not been achieved on host molecules containing the crown ether ring. The crown ether segment was then successfully combined with azobenzene in order to photocontrollably bind metal ions.[1] It is thought that photocontrolled binding and transportation activities resided mainly in the photoresponsive azo crown ethers. Access to a new thioindigo crown ether family is thus of great importance. Much effort has also focussed on the photoresponsive thioindigo derivatives[2,3] containing variable lengths of oxyethylene chains but the thioindigo containing cyclic crown ether has remained unexplored. Here, we describe the thioindigo crown ether.

**1c** was prepared as previously reported.[4] Using 7,7′-bis [2-{2-(2-mercaptoethoxy)ethoxy}ethoxycarbonyl] thioindigo we prepared **1b**† by adding chloranil directly without prior irradiation. The product was purified and fully characterised.

A Corey–Pauling–Koltun (CPK) model building of *trans*-**1b** showed a rigid structure, compared with that of *trans*-**1c**. The $-CH_2-$ groups of the *trans* isomer span over the C=C double bond and the benzene ring and are thus restricted, giving split signals of the protons. The side chain protons of the photoinduced *cis* isomer lie far away from the effect of benzene ring current and the free convolution of $-CH_2-$ brings about the resonance equilibrium. The protons of the *cis* isomers show signals in only three clusters instead of seven splitted clusters. The NMR results corroborate the conclusion derived from the CPK model.

*Trans*/*cis* configurational changes of thioindigo derivatives[2,3] is well known. Similar configurational changes for the compound **1** were also observed, Scheme 1. Configurational changes from *trans*-to-*cis* and *cis*-to-*trans* **1** were done by irradiation with 550 and 480 nm light, respectively. The absorption maximum ($\lambda_{max}$) for the *trans* forms by **1b** and **1c** were found to be 547 and 539 nm and that for the *cis* forms 480 and 488 nm respectively, Fig. 1. The configurational change of **1** which occurred with *trans*/*cis* isomerisation, was used in solvent extraction and the transportation of metal ions through organic membranes.

In solvent extraction experiments the ion binding ability was estimated by the anaerobic solvent extraction of metal salts of 8-anilinonaphthalene-1-sulfonate (ANS) from water to 1,2-dichloroethane at 25 °C. The extractibility was determined by the partition of ANS between the aqueous and the organic phase. The results of the extraction of ANS with **1** are summarised in Table 1. Extraction of metal ions by the *trans* isomers of **1b** was always zero, showing that the *trans* isomer can not form a cavity that can hold metal ions whereas the photoinduced *cis* isomers can. Examination of Table 1 reveals that photoisomerisation from *trans* to *cis* increased the extractibility with no change in selectivity. It is noteworthy to mention that compounds **1b** and **1c** exhibited very low affinity towards heavy metal ions such as $Hg^{2+}$, $Cd^{2+}$, $Cu^{2+}$, $Co^{2+}$, and $Ag^+$, in contrast to the alkali metal ions. It is well known that sulfur in a crown ring plays an important part in the binding of heavy metal ions, such as $Hg^{2+}$ and $Ag^+$.[5,6] Cooperative ligation with **1** and heavy metals was not found. Prior to transportation we evaluated the quantities of metal ions in both organic and aqueous phases by photoirradiation in a test tube. Using a photosignal at 550 nm for one min the photo generated *cis*-**1b** extracted about 7% of $Cs^+$ into the organic phase in two h. After two h of extraction the test tube was kept dark with constant stirring and it was found that



**1**
*trans*

**b**; *n* = 2
**c**; *n* = 3

*cis*

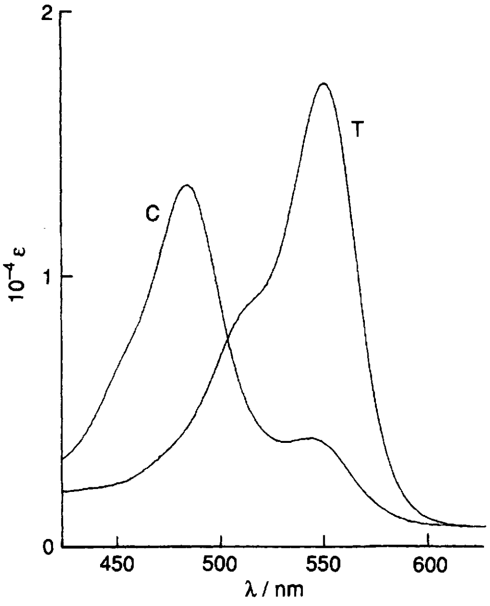


**Fig. 1** Absorption spectra of **1b** in 1,2-dichloroethane. T (*trans*) and C (*cis*) are the photostationary state spectra under irradiation with 480 and 550 nm light respectively.

**Table 1** Extraction of metal salts of ANS with **1**[a]

| Carrier | Extraction/% | | | | |
|---|---|---|---|---|---|
| | $Li^+$ | $Na^+$ | $K^+$ | $Cs^+$ | $Ca^{2+}$ |
| *trans* **1b** | trace | trace | trace | trace | trace |
| *cis* **1b** | 2.2 | 4.6 | 5.2 | 6.5 | 3.5 |
| *trans* **1c** | 2.9 | 3.3 | trace | 7.3 | 6.3 |
| *cis* **1c**[b] | 2.3 | 8.3 | trace | 13.0 | 10.7 |

[a] Organic phase, 1,2-dichloroethane solution containing **1**, (0.034 mmol dm$^{-3}$); aqueous phase containing a mixture of ANS (0.01 mmol dm$^{-3}$) and metal chloride (10 mmol dm$^{-3}$). [b] A mixture of *trans* and *cis* (40 : 60).

negligible amount of $Cs^+$ was released back to the aqueous phase in 24 h because of the extremely slow thermal isomerisation. On irradiation with 480 nm light for 30 s 29% of the captured $Cs^+$ was released back to the aqueous phase in two h. By alternate photoirradiation with light of 550 and 480 nm wavelength, metal ions were transported by **1b** within an H-type cell. The maximum amount of Cs,$^+$ 12%, was transported by **1b** repeating the capture and release cycle three times. The amount of $Ca^{2+}$ extracted into the organic phase, in one cycle, was 15.8%. The amount transported to the aqueous phase, was only 3.6%.

We reported earlier[3] that the rate of configurational change from *cis* to *trans* was considerably slower in the presence of $Ag^+$. Without the influence of any metal ions, the rate constant ($k$) for reversion of *cis*- to *trans*-**1b** at 50 °C *cis* was $4.1 \times 10^{-7}$ $s^{-1}$, about $10^2$ slower than that of thioindigo derivatives containing open chains.[3] Thus in the presence of any metal ions, thermal reversion can be expected to be slower.

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## Footnote

† $^1H$ NMR (300 MHz) data (δ in $CDCl_3$): *trans*-**1b** 8.36 (2H, d), 8.12 (2H, d), 7.46 (2H, t), 4.96 (2H, t, $\mathrm{OCOC}\mathit{H}\mathrm{H}$), 4.36 (2H, d, $\mathrm{OCOCH}\mathit{H}$), 4.07 (2H, m, $\mathrm{OCOCH_2C}\mathit{H}\mathrm{H}$), 3.71 (2H, d, $\mathrm{OCOCH_2CH}\mathit{H}$), 3.50 (4H, m, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2S}$), 2.60 (2H, m, $\mathrm{OCH_2C}\mathit{H}\mathrm{HS}$), 2.45 (2H, m, $\mathrm{OCH_2CH}\mathit{H}\mathrm{S}$); *cis*-**1b** 8.32 (2H, d), 8.08 (2H, d), 7.44 (2H, t), 4.64 (4H, t, $OCOCH_2$), 3.93 (8H, m, $CH_2OCH_2$), 3.05 (4H, t, $CH_2S$).

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