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# Highly Selective Transport of $Ag^+$ by a Macrobicyclic Host Containing a Bipyridine Moiety

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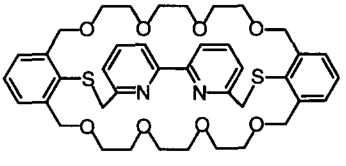
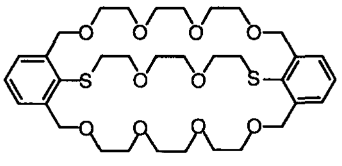
***Abstract:*** A macrocyclic polyether bridged by 2,2'-bipyridine group was synthesized and found to exhibit a very high $Ag^+$ ion selectivity compared to heavy metal ions in transport through an organic liquid membrane. © 1997 Elsevier Science Ltd.

Incorporation of a sulfur atom and a heterocyclic moiety into a macrocyclic ring or a rim of the cavity enhances the $Ag^+$ binding preference.[1-6] Control of the selective $Ag^+$ recognition was achieved using macrocycles containing thiol and disulfide groups prepared by the redox reactions.[5] The drastic change of the selectivity due to these simple modifications is of great interest for fundamental studies of host-guest chemistry. In addition, the high $Ag^+$ selectivity is important and necessary for technological applications such as photographic technology, recovery of $Ag^+$ from waste water, and $^{111}Ag$-based radioimmunotherapy.[6] Here we wish to report the synthesis of the bicyclic host **1** bearing a 2,2'-bipyridine moiety and its very high $Ag^+$ selectivity in cation transport through a liquid membrane.



**1**



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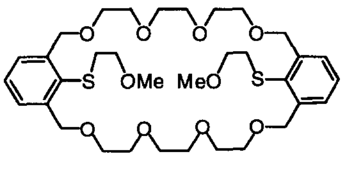

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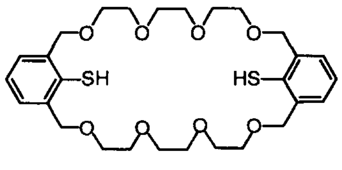
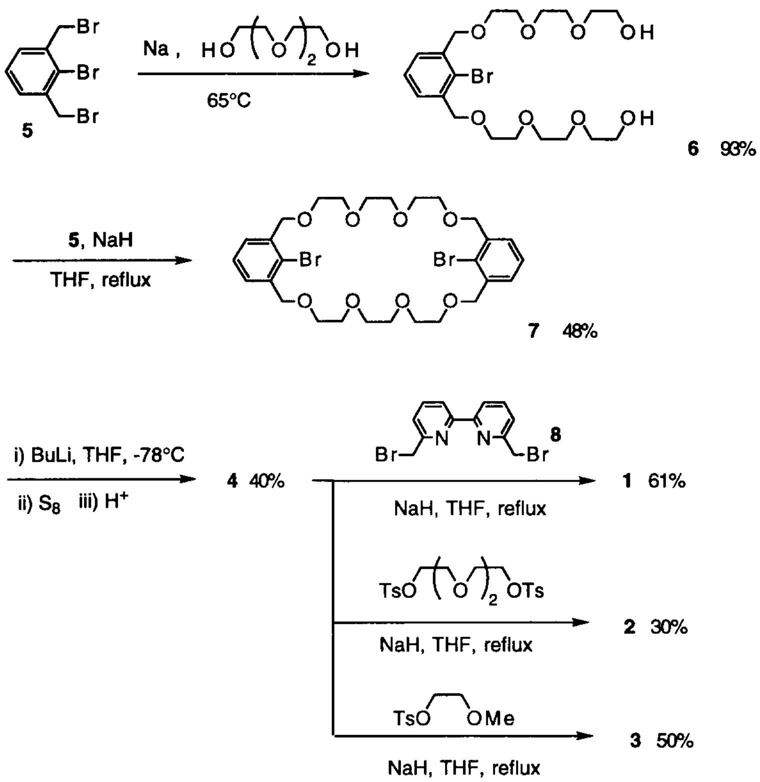


**4**

The diol **6** was prepared from the tribromide **5** and triethylene glycol, treating **6** with **5** gave the cyclic dibromide **7** (Scheme 1).[7] Dilithiation of **7** and treatment with elemental sulfur afforded the dithiol macrocycle **4**. Dithiol **4** was reacted with dibromide **8** in THF to give 2,2'-bipyridine-bridged host **1** in 61% yield. The hosts **2** and **3** were obtained in a similar way, namely, *via* the reactions of **4** with triethylene glycol ditosylate and 1-(*p*-toluenesulfonoxy)-2-(methoxy)ethane, respectively.

**Scheme 1.** Synthesis of hosts (**1**~**4**)



Cation transport through a liquid membrane (1,2-dichloroethane layer) using a dual cylindrical cell[8] showed that dithiol **4** transports $Ag^+$ selectively (Table 1). A small amount of $Pb^{2+}$ transported was the only other ion detected among heavy metal ions examined by atomic absorption spectroscopy. In the bipyridine host **1**, extremely high $Ag^+$ selectivity was achieved. The transport rate of $Ag^+$ is much higher (ca. 4 fold) than for **4**. Moreover, $Pb^{2+}$ was not observed in the receiving phase within the experimental errors. The other cations ($Mn^{2+}$, $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, $Zn^{2+}$, $Cd^{2+}$) were not carried at all as in the case of **4**. In the case of an acidic solution of $AgNO_3$ in aq $HNO_3$ (0.1 mol $dm^{-3}$) employed as an source phase, the amount of transported $Ag^+$ was reduced compared to an aqueous solution of $AgNO_3$ in deionized water, although the difference between the chemical potentials of the source and receiving phases increased under the acidic conditions. These results strongly suggest that the nitrogen atoms of the bipyridine nucleus in **1** participate in binding and transporting $Ag^+$. However, the macrocyclic host **3** containing two sulfide groups exhibits almost no ability for efficient or selective cation transport. In contrast, the bicyclic host **2** shows a relatively high $Ag^+$ selectivity comparable to that of **4**, but has no ability to $Pb^{2+}$ transport. Hence, the thiol groups of **4** play a considerably important role in the transport of $Ag^+$. In **2** the bicyclic structure consisting of three polyether chains and sulfur atoms are more favorable for the $Ag^+$ selectivity. Similarly, the remarkably high $Ag^+$ preference of **1** is probably due to both the bicyclic structure and effective coordination of the bipyridine to $Ag^+$. $^1H$ NMR titration unambiguously indicated the strong and almost quantitative coordination of the bipyridine to $Ag^+$ in a 1:1 complexation stoichiometry. In the presence of one equivalent of $Ag^+$ downfield shifts of protons located in the pyridine rings were observed (from 7.4 -7.5 ppm to 8.07 (d, J = 8 Hz) and 7.92 (t, J = 8 Hz) ppm in $CDCl_3$-$CD_3CN$ (9 : 1, v/v)). In aliphatic protons of the polyether chains, complexation gave rise to distinct shifts to a lower field, probably indicating interactions between the polyether groups with $Ag^+$.

Addition of $AgNO_3$ to **1** caused a bathochromic shift in uv-vis spectra from $\lambda_{max}$ 285 and 295 nm to 306 nm with a isosbestic point at 302 nm, consistent with the conversion of the free **1** to the $Ag^+$ complex without any intermediate.

The stability constant ($K_a$) of **1** and $Ag^+$ was determined by spectral changes at 327 nm with a non-linear-least-square method to be $K_a$ of $(2.5 \pm 0.3)\times10^4$ $dm^3$ $mol^{-1}$ in $CH_3CN$. Job plots using the absorbances at 327 nm also reveals the 1:1 complexation (Figure 1).

**Table 1.** Single ion transport for heavy metal ions[a]

| Host | Conc. of Metal Ion in the Receiving Phase ( x $10^{-5}$ mol $dm^{-3}$ ) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $Ag^+$ | $Mn^{2+}$ | $Co^{2+}$ | $Ni^{2+}$ | $Cu^{2+}$ | $Zn^{2+}$ | $Cd^{2+}$ | $Pb^{2+}$ |
| **1** | 62.7 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **1**[b] | 51.8 | - | - | - | - | - | - | - |
| **2** | 16.0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **3** | 1.8 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **4** | 15 | 0 | 0 | 0 | 0 | 0 | 0 | 1.3 |

[a] The values were determined after 24 h. source phase (Metal Nitrate (0.01 mol $dm^{-3}$) in dist. $H_2O$ (4 $cm^3$). receiving phase (dist. $H_2O$, 50 $cm^3$). organic phase (host ( 2 x $10^{-4}$ mol $dm^{-3}$) in $CH_2ClCH_2Cl$, 50 $cm^3$). 25 °C, stirring rate: 200 rpm. [b] $AgNO_3$ in 0.1 mol $dm^{-3}$ $HNO_3$

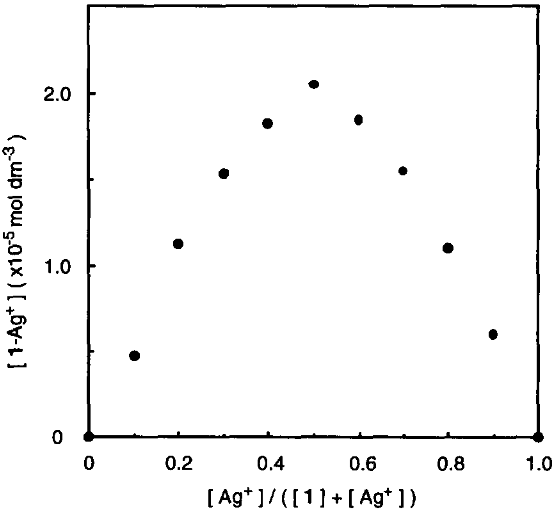


**Figure 1.** Job plots of **1**-$Ag^+$. [ **1** ] + [ $AgNO_3$ ] = 1.0 x $10^{-4}$ mol $dm^{-3}$, $\lambda_{obs}$ = 327.0 nm, $CH_3CN$, 25°C

The bipyridine macrocycle **1** shows a high $Ag^+$ transport selectivity obviously due to the coordination of the bipyridine ring and its bicyclic structure. We are currently preparing crystals of **1**-$Ag^+$ for X-ray crystallography to clarify the geometry of the ligand and to increase binding strength for practical applications.

**Acknowledgment**

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7 All new compounds had spectroscopic data (IR, NMR and mass spectrum) consistent with the assigned structure. The details of the synthesis and characterization of new compounds reported here will be described in a full paper.
Spectral Data for **1**: $^1$H NMR (500 MHz, $CDCl_3$-$CD_3CN$ = 9:1): $\delta$ = 3.25-3.35 (m, 16H), 3.43(t, J = 5 Hz, 8H), 4.28(s, 4H, $ArCH_2$(Bpy)), 4.50(s, 8H, $ArCH_2O$-), 7.00 (d, J = 7 Hz, 2H), 7.15-7.35 (m, 6H), 7.4-7.5 (m, 4H); $^{13}$C NMR (100MHz, $CDCl_3$): $\delta$ = 41.7, 69.3, 70.25, 70.37, 72.0, 118.9, 122.6, 127.9, 128.4, 131.0, 136.8, 143.5, 154.6, 157.7; FABMS, m/e 749 ($[M+H]^+$). X-ray crystallographic data of **1**, which will be reported elsewhere, also ascertain the structure.

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