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Synthesis of Mono-, Bis-, and Tris-dithiapentaoxacrown Ethers: Complexation Studies with Some Metal Picrates

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Dithiatetraoxa– 1a, dithiapentaoxa– 1b, dithiahexaoxa– 1c, bis-dithiapentaoxa– 18, and tris-dithiapentaoxa–crown ethers 22 were synthesized in order to study the complexation of bis- and tris-thiacrown ethers in which the cycles are bounded to the same carbon atom, with metal picrates. Measurements of the affinity of metal ions (Cs^+, Rb^+, Ba^{2+}, K^+, Ag^+, Pb^{2+}, Sr^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}), to these molecules represented by extractability, defined by equation 1, showed that Ag^+ was strongly attracted by 1a (95%), 1b (94%), 1c (65%), 18 (193%), and 22 (270%). It appeared that the extractability increased linearly with the number of cavities in the molecule (*cf.* Mono– 1b, bis– 18, and tris-crown ethers 22). However, extractabilities of Pb^{2+} shown by only 21-membered 1b, 18, and 22, in spite of much lower values than those of Ag^+, were not additive, For noncompetitive transport of metal ions (Ba^{2+}, Ag^+, Pb^{2+}) through a liquid membrane, 1a favored transport of Ag^+ over Pb^{2+}. However 1b–c favored transport of Pb^{2+}. The tendency of the former may be responsible for negligible extractability of Pb^{2+} due to the size of the cavity, whereas the latter may be attributable to a weaker affinity for Pb^{2+} than for Ag^+, so that Pb^{2+} associated weakly with 1b–c is transported readily. For competitive transport of metal ions (Ba^{2+}, Ag^{2+}, Pb^{2+}, Cu^{2+}) by dithiacrown ethers 1a–b, and 22, only transport of Pb^{2+} occurred predominantly. The degree of complexation obtained based on the comparison of ^1H NMR spectra of 1a–c, 18, 22 and the corresponding Ag^+ complexes was almost the same as those obtained from the solvent extraction.

Keywords: Dithiapentaoxacrown ethers, metal picrates, extractability, liquid membrane, jobs plot

INTRODUCTION

The complexation of macrocylic polyethers or crown ethers to alkali metals and other cations has been well documented [1]. Much attention has devoted to modulating the binding affinity of crown ethers by introducing a polyether side chain, amide bonds, substituted hydrazone group, or an alkylthio group into the crown ring with the expectation of synergistic coordination of the ring oxygens and the additional oxygen [2], nitrogen [3], or sulfur [4] atoms of the side chain to metal ions. In addition, bis-(crown or thiacrown) derivatives consisting of two monocycles connected by a hydrocarbon chain [5], alkene [6], azo unit [7], or a metallocene redox center [8] to form 2:1 (crown ether unit/cation) sandwich-type complexes with particular cations have recently received much attention.

Although crown and thiacrown ethers having various cavity sizes have been synthesized [1(c), 9], bis-15-crown-5 [10], bis-18-crown-6

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[11], and their corresponding thiacrown ethers [5(f)] have been exclusively employed for studies on complexations with alkali, alkaline earth, and heavy metal ions. However, no complexation study on bis- and/or tris-crown and thiacrown ethers bonding to the same carbon atom has been reported. This work was undertaken to determine if the binding properties exhibited by a monothiacrown ether would be additive in the cases of bis- and tris-crown ethers. It was our hope that remarkably high extractability and transport selectivities for heavy metal ions such as Ba^{2+}, Ag^{+}, and Pb^{2+} which are of interest in relation to the environment and human toxicity would be observed from complexation study.

In order to prepare dithiatetraoxa – **1a**, dithiapentaoxa – **1b**, dithiahexaoxa – **1c**, bis-dithiapentaoxa – **18**, and tris-dithiapentaoxa-crown ethers **22** where each have a 2-phenylthiodiphenyl sulfide unit as a part of the chain consisting of the cycle, 5-arylthianthreniumyl perchlorates were used as starting materials. The desired macrocyclic compounds were synthesized by a series of reactions. Complexation of the compounds with foregoing heavy ions and other metal ions were studied. The results are described herein.

RESULTS AND DISCUSSION

Synthesis of 1a–c, 18, and 22

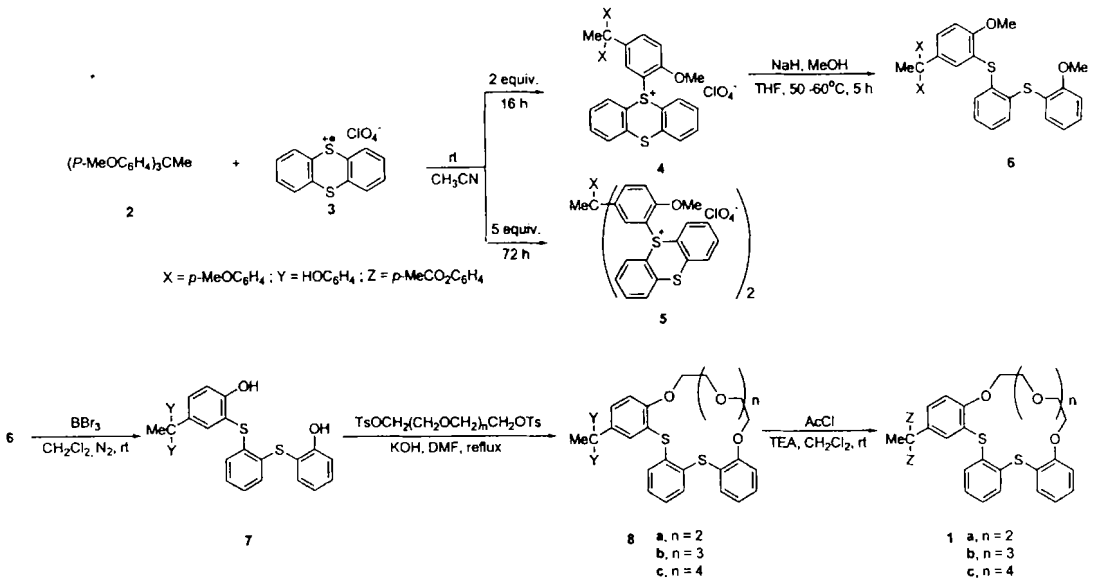
1,1,1-Tris(*p*-anisyl)ethane (**2**) was treated with thianthrene cation radical perchlorate (**3**) [13] (2 molar equivalents) in dried acetonitrile at room temperature for 16 h to give thianthreniumyl perchlorate **4** (64%). However, treatment of **2** with **3** (5 molar equivalents) for 72 h afforded bis-thianthreniumyl perchlorate **5** (80%). The reaction of **4** with sodium methoxide, prepared *in situ* by addition of sodium hydride in methanol, in tetrahydrofuran at 50 to 60°C for 5 h under nitrogen atmosphere gave tetramethoxy compound **6** (62%) [13]. Demethylation of **6** with boron tribromide in dichoromethane at room temperature under nitrogen atmosphere gave phenolic compound **7** (82%) Treatment of **7** with triethylene glycol ditosylate in the presence of potassium hydroxide in dimethylformamide for 2.5 h at reflux gave dithiatetraoxacrown ether **8a** (36%). Similar treatment of **7** with tetra- and pentaethylene glycol ditosylates gave dithiapentaoxa – **8b** (45%) and dithiahexaoxa-crown ether **8c** (31%), respectively.

In order to confirm that the cyclization was achieved in the desired manner, the mesylation reactions of **7** and **8b** with methanesulfonyl chloride in the presence of triethylamine (TEA) in dichloromethane at room temperature were carried out (Scheme 2). Comparison of ^{1}H NMR spectrum of **9** with that of mesylated compound **10** clearly indicates that the para hydroxyphenyl groups without the sulfur atom of **7** are intact after the cyclization.

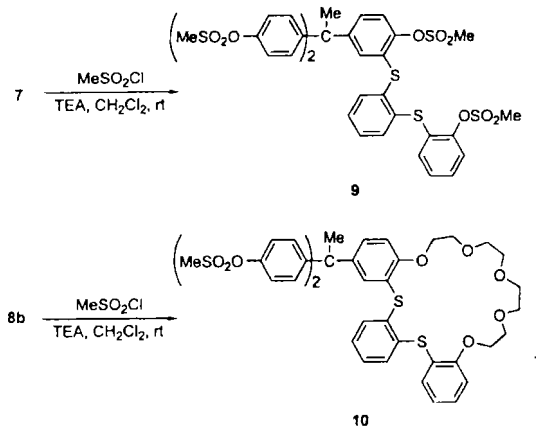
The hydroxy groups of compounds **8** were protected by acetylation using acetyl chloride to give acetylated compounds **1** (**1a**, 90%; **1b**, 66%; **1c**, 91%).

Using compound **5**, compounds **11** (53%) and **12** (87%), which are analogous to compounds **6** and **7**, respectively were prepared by the same methods. However, the cyclization of **12** with tetraethylene glycol ditosylate under the same conditions as **8** gave a complex mixture. Attempted cyclization of **12** under other conditions (K_2CO_3, DMF, Δ; Cs_2CO_3, DMF) failed. Therefore compound **14**, in which one of the methoxy groups of **2** was substituted for a methyl group, was prepared in order to avoid a possible interference arising from the presence of an extra phenol group at the cyclization stage.

The reaction of *p*-tolylacetophenone (**13**) with anisole (2 molar equivalents) in a mixture of concentrated H_2SO_4 and HOAc gave 1,1-bis (*p*-anisyl)-1-(*p*-tolyl)ethane **14** (20%), which was treated with **3** (5 molar equivalents) under the same conditions as for the preparation of **5** to give bis-thianthreniumyl perchlorate **15** (70%) (Scheme 3). Starting from compound **15**, compounds **16** (59%) and **17** (100%) were obtained by applying the same methods as those used for

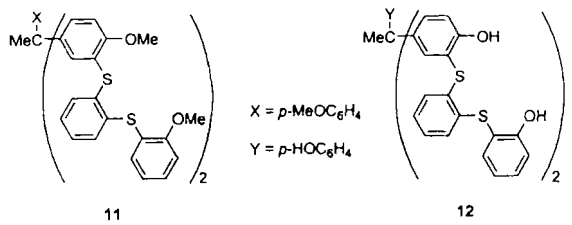


SCHEME 1



SCHEME 2

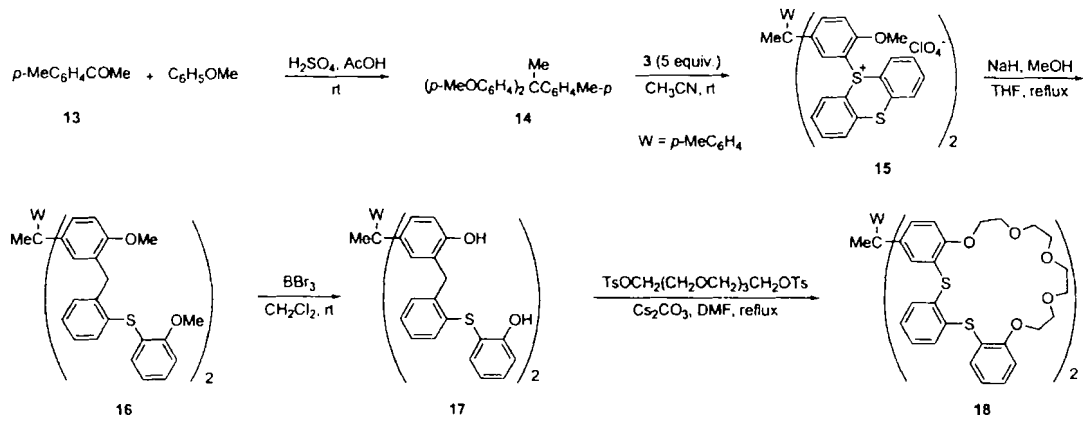
6 and 7. Cyclization of **17** using tetraethylene glycol ditosylate in the presence of cesium carbonate in dimethylformamide gave bis-dithiapentaoxacrown ether **18** (53%).



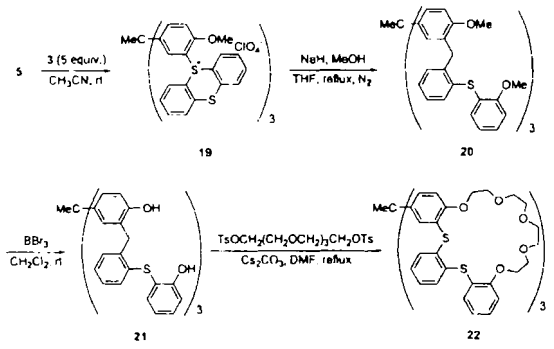
Compound **5** was treated with **3** (5 molar equivalents) under the same conditions as for **15** to give tris-thianthreniumyl perchlorate **19** (47%) (Scheme 4). Starting from **19**, compounds **20** (51%), **21** (90%), and **22** (24%) were obtained by applying the same methods as for **15** through **18**, respectively.

Solvent Extraction for Metal Ions

The affinity of metal ions to compounds **1a–c**, **18**, and **22** was examined by the mixing of a deionized aqueous solution of a metal picrate which was prepared by literature procedures, [14] with each of the host compounds in chloroform. To an aqueous metal picrate (5×10^{-3} M, 2 mL) was added a solution of host compound in chloroform (1×10^{-3} M, 2 mL), which was vigorously stirred and then kept at constant temperature for an appropriate time. From the UV absorption of the aqueous metal picrate measured at 354 nm, one can determine the concentration of the metal picrate transferred to the chloroform layer. Likewise, the concentration of the guest molecules transferred to the plain chloroform layer without the host molecules can



SCHEME 3



SCHEME 4

be determined. The extractability defined as Eq. (1) [4(a)] is calculated for sulfides **1a–c**, **18**, and **22** and is tabulated in Table I.

$$\text{Extractablilty}(\%) = ([M_{aq}] - [M_t])/[H_0] \times 100 \quad (1)$$

where $[M_{aq}]$ is the concentration after the initial concentration of picrate in the aqueous phase minus the concentration of picrate transferred into the plain chloroform phase, and $[M_t]$ is the concentration of picrate in the aqueous phase after extraction. $[H_0]$ is the concentration of the host molecule. The Eq. (1) means that the maximum extractabilities by mono- **1**, bis- **18**, and tris-dithiapentaoxacrown ethers **22** become 100, 200, and 300%, respectively.

Table I shows that the affinity of Ag^+ (ionic radius = 1.26 Å) [15] is striking regardless of the ring size of the host compounds **1a–c** which are 18-, 21- and 24-membered cyclic compounds, respectively. The results are consistent with the reports in which Ag^+ interacts strongly not only with 18-crown-6, 21-crown-7 and 24-crown-8 [12(a), 16] but also with those of the corresponding sulfur containing compounds [10(c), 12(b), 17(a)–(c)]. However, the extractability of **1c** (65%) is smaller than those of **1a** (95%) and **1b** (94%). The lager cavity of **1c** may be responsible for the smaller extractability of **1c**.

TABLE I Solvent extraction of metal ions

host	Extractability (%)[a]									
	Cs^+	Rb^+	Ba^{2+}	K^+	Ag^+	Pb^{2+}	Sr^{2+}	Ca^{2+}	Cu^{2+}	Mg^{2+}
1a	0	5	2	0	95	1	0	0	5	0
1b	0	0	5	5	94	54	0	0	1	1
1c	6	10	6	2	65	8	2	0	1	4
18	7	2	14	4	193	77	0	4	1	2
22	0	2	11	3	270	81	0	0	0	0

[a] Organic phase ($CHCl_3$); [host] = 1×10^{-3} M. Aqueous phase; [metal picrate] = 5×10^{-3} M. Ionic radius is on the decrease from the left to the right.

It is interesting to note that Pb^{2+} (ionic radius = 1.20 Å) which has a similar ionic radius as Ag^+, is extracted significantly by **1b** (54%), whereas its extractabilities by **1a** (1%) and **1c** (8%) are negligible. The results indicate that the donor atoms comprising the cavity play an important role for the differentiation in extractabilities as suggested [4(a), 18]. It is noteworthy that a 18-membered **1a** shows essentially no extractabilities with Pb^{2+} as well as Ba^{2+} (ionic radius = 1.34 Å) and Sr^{2+} (ionic radius = 1.12 Å), which is in contrast with the observation that Pb^{2+} in a solution containing Pb^{2+}, Sr^{2+}, and Ba^{2+} is selectively transported by dibenzo-18-crown-6 [18].

The extractabilities of Ag^+ by mono- **1b** (94%) bis- **18** (193%), and tris-dithiapentaoxacrown ethers **22** (270%) increase linearly with the number of the cavities in the molecule, whereas that of Pb^{2+} by **18** (77%) increases somewhat compared with that of **1b** (54%). The extractability of Pb^{2+} by **22** (81%) is essentially the same as that of **18** (Tab. I). The results clearly indicate that the affinity for Ag^+ by 21-membered mono-, bis-, and tris-dithiapentaoxacrown compounds is additive, so that the complexation of Ag^+ by one cavity does not interfere with the complexation by the other cavities in the molecule with respect to the metal dipole interaction involved and the possible conformational changes due to the complexation. In other words, Ag^+ is expected to lie in the center of each cavity due to a strong interaction with the donor atoms, and even the three cavities of **22** occupy the space without any steric congestion among the Ag^+ ions in the molecule. Therefore, the selectivity for Ag^+ by **22** in extractability would be the greatest. In contrast, the affinity of Pb^{2+} is not additive, presumably because of a relatively weak interaction with the donor atoms of the cavities and a metal-dipole repulsion produced by an interaction between a dipositive ion and donor atoms. As a result, the extractability of **18** increases somewhat compared with that of **1b** but is comparable to that of **22**.

Transport of Metal Ions through a Liquid Membrane

Transport experiments were performed at room temperature in a U-tube glass cell containing ionophore (1×10^{-3} M) in chloroform (10 mL) in the base. For noncompetitive transport, a solution of a metal picrate, *i.e.*, Ag^+, Pb^{2+}, and Ba^{2+} in deionized water, whose concentration was 5×10^{-3} M, and deionized water (5 mL) were placed in each tube arm. After the membrane phase was constantly stirred for 40 h, the concentration of a metal ion in the aqueous receiving phase was determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). Blank experiments (no host present) were performed for each source phase salt solution to determine membrane leakage. The results are listed in Table II. For competitive transport, a solution of four metal (Ag^+, Pb^{2+}, Cu^{2+}, Ba^{2+}) picrates in the same solvent, whose concentrations were 2×10^{-3} M, was employed under the same conditions as for noncompetitive transport. The results from non- and competitive transports are summarized in Tables II and III, respectively.

TABLE II Noncompetitive transport of heavy metal ions by **1a–c**

	[metal ion] in the receiving phase ($\times 10^{-6}$M) (after 40 h)		
	Ba^{2+}	Ag^+	Pb^{2+}
blank	1.26	0.07	0.00
1a	0	292.9	80.5
1b	234.5	283.8	1079.3
1c	139.8	233.5	445.9

TABLE III Competitive transport of heavy metal ions by **1a–c 18, 22**

	[metal ion] in the receiving phase ($\times 10^{-6}$M) (after 40 h)			
	Ba^{2+}	Ag^+	Pb^{2+}	Cu^{2+}
1a	0.0	14.0	33.0	0.0
1b	75.7	36.2	349.0	0.0
1c	85.9	137.0	101.0	0.0
18	119.0	9.5	443.0	1.1
22	99.5	7.4	352.0	4.7

For noncompetitive transport by **1a**, Ag^+ and Pb^{2+} are transported. Transport of Pb^{2+} is unusual in view of the negligible extractabilities of **1a** to Pb^{2+} as well as Ba^{2+} (Tab. I), which indicates that **1a** interacts somehow with Pb^{2+}. Table II shows a better transport of Pb^{2+}, over both Ba^{2+} and Ag^+, by **1b** and **1c** rather than **1a**. The higher values in transport of Pb^{2+} over Ag^+ by **1b** and **1c** may be attributable to a weaker affinity of Pb^{2+} than Ag^+ to 21 and 24-membered **1b-c** as shown by their extractabilities (Tab. I). As a result, Pb^{2+} associated weakly with the host molecules is expected to be transported more readily than Ag^+ associated strongly with the host molecules. In contrast, the opposite tendency in transport of Ag^+ and Pb^{2+} by **1a** may be due to a negligible extractability of Pb^{2+}. In other words, the concentration of Pb^{2+} associated with **1a** is very small. Consequently the extent of the association with **1a** seems to be a controlling factor in determining the order of magnitude of transport. This view may be supported by the data in which the concentrations of Pb^{2+} transported by **1b** and **1c** are four and two times greater than those of Ag^+, respectively, whereas the extractabilities of Ag^+ by **1b** and **1c** are two and eight times greater than those of Pb^{2+}, respectively (Tab. I).

It is noteworthy that transport of Ba^{2+} by **1b** is comparable to that of Ag^+, and that transport by **1c** is far less that of Ag^+ in spite of negligible extractabilities of Ba^{2+} by **1a–c**. These results indicate that the too small size of the cavity of a 18-membered **1a** may be responsible for the essential lack of interaction with Ba^{2+}. However, there is a significant interaction between Ba^{2+} and both **1b** and **1c**, but the interaction does not seem to be strong and thus the concentrations of Ba^{2+}–**1b** and Ba^{2+}–**1c** complexes are not sufficient to be detected by both UV and NMR spectroscopies.

For competitive transport of Ba^{2+}, Ag^+, Pb^{2+} and Cu^{2+} (Tab. III), transport of Pb^{2+} by **1a–b**, **18**, and **22** occurs predominantly. Transports of Pb^{2+} by 21-membered mono– **1b**, bis– **18**, and tris-dithiapentaoxacrown ethers **22** are especially striking. Tables II and III show that transport of Pb^{2+} by **1b** occurs eight times and four times greater than that of Ag^+ in competitive and noncompetitive transports, respectively, which means that a better transport of Pb^{2+} occurs in competitive transport rather than in noncompetitive transport. This result is consistent with that previously reported [18].

Apart from the tendency observed from noncompetitive transports of Ba^{2+} and Ag^+ by **1b** and **1c** (Tab. II), Ba^{2+} was transported better than Ag^+ by **1b** in competitive transport, but the opposite tendency was observed by **1c** in noncompetitive transport. It is difficult to explain the observed disparity shown by **1b** and **1c** in non- and competitive transports.

^1H NMR Spectral Changes by Complexation with Ag^+

As mentioned in the solvent extraction for metal ions, a solution of a host compound in chloroform was mixed with an aqueous solution of silver picrate for an appropriate time. The Ag^+-host complex for ^1H NMR study was obtained by removal of the solvent from the chloroform layer. ^1H NMR spectra of **1a–c**, **18**, and **22** were compared with those of the Ag^+-host complexes in order to see the extent to which Ag^+ affects the chemical shifts of the ^1H NMR spectra of the uncomplexed host compounds. The number of protons corresponding to each peak exhibited by the Ag^+–**1a–c** complexes was determined by comparing the intensity of the ester methyl signal of each complex, since the chemical shifts of the ester methyl protons of **1a** and its Ag^+–**1a** complex are the same, which in turn suggests that the interaction between the ester carbonyl oxygen and/or the alcohol oxygen and Ag^+ is absent or not strong enough to be detected by ^1H NMR spectroscopy. The intensity of a singlet at 8.72 ppm exhibited by a picrate, coupled with that of the ester methyl signal at 2.29 ppm, indicates that 95% of **1a** exists as a Ag^+–**1a**

complex under the conditions of the extractability experiment. The result was exactly the same as that obtained from the extractability experiment (Tab. I). Compound **1a** exhibited three multiplets corresponding to four protons each at 3.65, 3.78, and 4.12 ppm, which were split into five multiplets, corresponding to 2H, 4H, 2H, 2H and 2H, at 3.89, 3.95, 4.02, 4.29 and 4.52 ppm, respectively, in the ^{1}H NMR spectrum of the Ag^+–**1a** complex. The down field shifts of the methylene proton signals with a broader range [12(c), 19] indicate that Ag^+ interacts with four oxygen donors in the molecule, while is in good agreement with the excellent extractability of Ag^+ by **1a**.

Compound **1b** exhibited two multiplets at 3.78 (12H), and 4.14 (4H) ppm, whereas the Ag^+–**1b** complex exhibited four multiplets at 3.27 (2H), 3.69 (2H), 3.90 (10H), and 4.37 (2H) ppm. The upfield shifts of two multiplets *i.e.*, 3.27 and 3.69 ppm shown by the complex suggest that the comformations around the cavities of Ag^+–**1a** complex and Ag^+–**1b** complex are not the same, although **1a** and **1b** show almost the same extractabilities. The intensities of two singlets at 8.50 ppm and 2.29 ppm exhibited by a picrate and an ester methyl group, respectively, indicate that 94% of **1b** exists as a Ag^+–**1b** complex, which is in accord with the extractability shown by **1b**. Compound **1c** exhibited two multiplets at 3.60 to 3.78 (16H) and 4.16 (4H) ppm, which were split into a much more complicated multiplet (3.45–4.29 ppm) when **1c** makes a complex with a silver picrate. One possible cause for the complexity of the methylene proton signals may originate from the size of the cavity which is too large for a strong interaction with Ag^+. At this moment, it is hard to say how many oxygen atoms consisting of the cavity interact with Ag^+, in view of the flexible comformation of the cavity. A single at 8.59 ppm exhibited by the Ag^+–**1c** complex suggests that 79% of **1c** exists as a Ag^+–**1c** complex. The value is 12% higher compared with that obtained from the extractability experiment.

Bis-cyclic compound **18** exhibited three multiplets assignable to methylene protons at 3.72 (24H), 4.01 (4H), and 4.08 (4H) ppm. The multiplets are split into five multiplets which appear at 3.35 (4H), 3.64 (4H), 3.79 (16H), 4.04 (4H) and 4.10 (4H) ppm when **18** makes a Ag^+–**18** complex. Similarly, tris-cyclic compound **22** and its Ag^+–**22** complex exhibited three multiplets at 3.81 (36H), 4.08 (6H), and 4.16 (6H) ppm and five multiplets at 3.46 (6H), 3.66 (12H), 3.76 (18H), 3.97 (6H), and 4.12 (6H) ppm, respectively, which are assignable to methylene protons. The splitting patterns of a Ag^+–**18** complex and a Ag^+–**22** complex, including the downfield shifts of the first few multiplets to 3.7–3.8 ppm, are similar to the aspect shown by a Ag^+–**1b** complex. This in turn suggests that the complexation of Ag^+ by one cavity of bis– **18** and tris– **22** cyclic compounds does not interfere with the complexation of the rest of the cavities in the molecule. In fact, the intensities of two single, one at 8.45 ppm due to a picrate and one at 1.94 ppm assignable to methyl protons on sp^3 carbon atom of **18**, indicate that 191% of **18** exists as a Ag^+–**18** complex. The same comparison between the intensities of two singlets at 8.44 ppm and 1.97 ppm indicates that 300% of **22** exists as a Ag^+–**22** complex. The value 191% is close to the extractability 193%, but the value 300% is somewhat higher than the extractability 270%. The values determined on the basis of ^{1}H NMR spectroscopy are somewhat variable depending on how the measurement of an intensity of a multiplet is made. Consequently, the variation becomes large especially for a compound with weak broaden multiplets.

Jobs Plot

Seven different concentrations of **1b** in chloroform and the same number of differing concentrations of silver picrate in water were prepared. A Jobs plot was obtained by mixing five milliliters of two different solutions to become 1.0×10^{-3} M. Figure 1 shows that the highest absorbance is gained when **1b** (5.8×10^{-4} M) is

mixed with an aqueous silver picrate (4.9×10^{-4} M). The result clearly indicates that **1b** makes a 1:1 complex with a silver picrate. Figure 2 shows the changes of the concentrations of silver picrate trapped by **1a–c** whose concentrations are 9.5×10^{-4} M. The concentration of Ag^+ extracted by **1a** increases rapidly at the beginning in which the ratio, $[Ag^+]/[H_0]$, is small. As the ratio approaches 1, the concentration of Ag^+ extracted increases slowly until a plateau is finally reached. When the ratio becomes 1, the concentration of Ag^+ extracted by **1a** is smaller than the concentration of **1a**. The result is in accord with the excellent extractability (95%) shown by **1a**. The same phenomena were observed from **1b**, which is also consistent with 94% of the extractability shown by **1b**. However, the concentration of Ag^+ extracted by **1c** increases slowly. In fact, the beginning point of the plateau is not clear. The result indicates that **1c** does not readily make a complex with Ag^+, which is in agreement with the low extractability (65%).

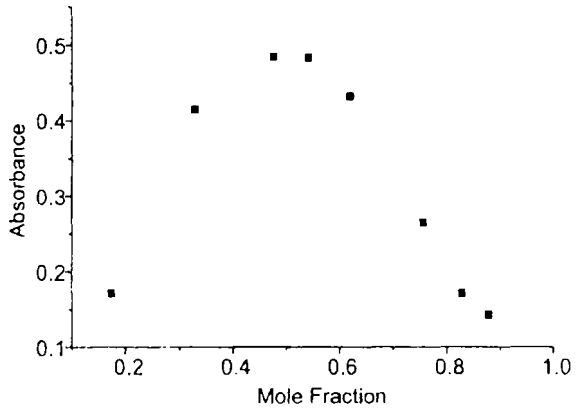


FIGURE 1 Absorbance of Ag^+–**1b** complex *versus* the mole fraction [**1b**]/([**1b**] + [Ag^+]) at constant [**1b**] + [Ag^+].

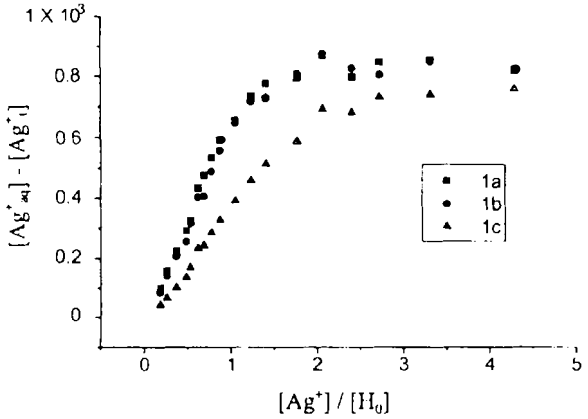


FIGURE 2 The concentration of Ag^+ extracted by the host molecules **1a–c** (1×10^{-3}) *versus* the ratio $[Ag^+]/[H_0]$.

CONCLUSION

Extractabilities of Ag^+ by 21-membered mono- **1b**, bis- **18**, and tris-dithiacrown ethers **22** increase linearly with the number of the cavities in the molecule, meaning that the complexation of Ag^+ by one cavity does not interfere with the complexation of the remaining cavities in the molecule. Extractability of Ag^+ by an 18-membered **1a** is essentially the same as that by **1b**, whereas a 24-membered **1c** shows a low extractability of Ag^+, presumably due to a too large cavity for the accommodation of Ag^+. The same tendency toward complexation is observed from ^1H NMR study.

For noncompetitive transport of metal ions (Ba^{2+}, Ag^+, Pb^{2+}), **1a** favors transport of Ag^+, whereas **1b** favors transport of Pb^{2+}. The former may be responsible for a negligible extractability of Pb^{2+} and the latter may be attributable to a weak affinity for Pb^{2+} than for Ag^+ so that Pb^{2+} is expected to be transported more readily than Ag^+.

For competitive transport by metal ions (Ba^{2+}, Ag^+, Pb^{2+}, Cu^{2+}) by **1a–b**, **18**, and **22**, transport by Pb^{2+} occurs predominantly regardless of the size of the cavities.

A Jobs plot shows that **1b** makes a 1:1 complex with Ag^+.

EXPERIMENTAL SECTION

The ^1H NMR spectra were recorded at 80 or 300 MHz in $CDCl_3$ or DMSO-d_6 solution

containing Me_4Si an internal standard. IR spectra were recorded in KBr or thin films on KBr plates. Elemental analyses were determined by the Korea Basic Science Center. Inductively Coupled Plasma-Atomic Emission spectral data and Mass Spectra were determined by Inter-University Center for Natural Science research Facilities. Column chromatography was performed using silica gel (230–400 mesh, Merck). Melting points are uncorrected.

5-[5-{1,1-(Di-4-anisyl)ethyl}-2-methoxy] phenylthianthreniumyl perchlorate (4)

To a solution of thianthrene cation radical perchlorate (**3**) (1.00 g, 3.17 mmol) in dry acetonitrile (50 mL) was added 1,1,1-tri(4-anisyl)-ethane (**2**) (550 mg, 1.58 mmol). The mixture was stirred at room temperature for 40 h. Removal of the solvent *in vacuo* gave a residue which was chromatographed on a silica gel column (10 × 3 cm). Elution with *n*-hexane gave thianthrene (369 mg, 1.71 mmol). Elution with EtOAc gave unreacted **2** (72 mg, 0.21 mmol). Elution with acetone gave a yellowish compound **4** (778 mg, 74%): mp 207–208°C (acetone); ^{1}H-NMR (DMSO-d_6, 300 MHz): 1.96 (*s*, 3H, CCH_3), 3.78 (*s*, 6H, OCH_3), 3.95 (*s*, 3H, OCH_3), 5.83 (*s*, 1H, ArH), 6.67 (*m*, 8H, ArH), 7.32 (*d*, J = 8.80 Hz, 1H, ArH), 7.78 (*m*, 5H, ArH), 7.87 (*dd*, J = 7.67, 1.66 Hz, 2H, ArH), 8.33 (*dd*, J = 7.57, 1.65 Hz, 2H, ArH); IR (KBr): 3056, 2960, 2824, 1594, 1504, 1442, 1248, 1082 cm^{-1}. Anal. calcd for $C_{35}H_{31}ClO_7S_2$: C, 63.39; H, 4.71; S, 9.67. Found: C, 63.25; H, 4.72; S, 9.58.

2-[5-{1,1-(Di-4-anisyl)ethyl}-2-methoxyphenylthio] 2′-methoxydiphenyl sulfide (6)

To a suspension of NaH (160 mg, 6.67 mmol) in dry THF (50 mL) was added MeOH (214 mg, 6.67 mmol) at room temperature under nitrogen atmosphere. The mixture was stirred for 30 min, followed by addition of **4** (1.12 g, 1.69 mmol). The reaction mixture was stirred at 50°C to 60°C for 5 h and then cooled to room temperature. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (10 × 3 cm). Elution with a mixture of EtOAc and *n*-hexane (1:9) gave **6** (860 mg, 85%): mp 62–64°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.06 (*s*, 3H, CCH_3), 3.82 (*s*, 6H, OCH_3), 3.85 (*s*, 6H, OCH_3), 6.76 (*dd*, J = 6.78, 2.14 Hz, 4H, ArH), 6.84–7.07 (*m*, 11H, ArH), 7.64 (*m*, 4H, ArH); IR (neat) 3056, 2936, 2832, 1606, 1576, 1500, 1478, 1459, 1388, 1290 cm^{-1}; MS(EI) m/z 594 (M^+, 6.3%), 579 (8.3), 331 (22.6), 290 (56.8), 241 (19.3), 200 (52.2), 184 (37.2), 133 (100). Anal. calcd for $C_{36}H_{34}O_4S_2$: C, 72.70; H, 5.76; S, 10.78. Found: C, 72.65; H, 5.71; S, 10.65.

2′-Hydroxy-2-[5-{1,1-(di-4-hydroxyphenyl)ethyl}-2-hydroxyphenylthio]diphenyl sulfide (7)

To a solution of **6** (1.06 g, 1.78 mmol) in dried CH_2Cl_2 (50 mL) was added BBr_3 (1.78 g, 7.13 mmol) under nitrogen atmosphere. The mixture was stirred for 12 h at room temperature and then slowly poured to cold water (100 mL). The mixture was extracted with CH_2Cl_2 (30 mL × 5). The extracts were dried over $MgSO_4$. Evaporation of the solvent gave an oily residue which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of EtOAc and *n*-hexane (1:3) gave **7** (787 mg, 82%): oily liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.11 (*s*, 3H, CCH_3), 4.80 (*s*, 2H, OH), 6.46 (*s*, 1H, OH), 6.50 (*s*, 1H, OH), 6.74 (*dd*, J = 6.69, 2.14 Hz, 4H, ArH), 6.86 (*m*, 2H, ArH), 6.94–7.10 (*m*, 10H, ArH), 7.30 (*sd*, J = 2.38 Hz, 1H, ArH), 7.41 (*td*, J = 7.50, 1.67 Hz, 1H, ArH), 7.54 (*dd*, J = 7.76, 1.65 Hz, 1H, ArH); IR (neat): 3400, 2976, 1592, 1498, 1179 cm^{-1}; MS(EI) m/z 538 (M^+, 51.19), 523 (100). HRMS (EI): Calcd for $C_{32}H_{26}O_4S_2$ 538.1273, found 538.1270.

2,3,17,18-Dibenzo-5,6-[3-{1,1-(di-4-hydroxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16-tetraoxacyclooctadeca-2,5,17-triene (8a)

To a mixture of **7** (1.03 g, 1.30 mmol) and KOH (540 mg, 9.56 mmol) was added DMF (50 mL), followed by addition of a solution of triethylene glycol ditosylate (880 mg, 1.30 mmol) in DMF (30 mL) at room temperature. The mixture was heated at 120–130°C for 5 h. The cooled reaction mixture was poured into water (300 mL), which was acidified with 5% HCl. The aqueous solution was extracted with CH_2Cl_2 (100 mL × 5). The combined extracts were washed with a 5% HCl solution (50 mL × 8). Removal of the solvent *in vacuo* gave a residue which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of *n*-hexance and EtOAc (1:3) gave **8a** (530 mg, 42%); mp 210–212°C (EtOAc-*n*-hexane); ^{1}H-NMR (DMSO-d_6, 300 MHz): 2.00 (*s*, 3H, CCH_3) 3.45 (*m*, 4H, OCH_2), 3.61 (*m*, 4H, OCH_2), 4.07 (*m*, 4H, Ar-OCH_2), 6.63 (*m*, 2H, ArH), 6.64 (*d*, J = 8.52 Hz, 4H, ArH), 6.81 (*d*, J = 8.58 Hz, 4H, ArH), 6.94–7.14 (*m*, 7H, ArH), 7.39–7.47 (*m*, 2H, ArH), 9.28 (*s*, 2H, OH); IR (KBr): 3320, 2936, 1607, 1507, 1438 cm^{-1}. Anal. calcd for $C_{38}H_{36}O_6S_2$: C, 69.91; H, 5.56; S, 9.82. Found: C, 69.65; H, 5.53; S, 9.75.

2,3,17,18-Dibenzo-5,6-[3-{1,1-(di-4-acetoxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16-tetraoxacyclooctadeca-2,5,17-triene (1a)

To a mixture of **8a** (250 mg, 0.38 mmol) and triethylamine (117 mg, 1.15 mmol) in CH_2Cl_2 (20 mL) was added acetyl chloride (90 mg, 1.15 mmol) at room temperature. The mixture was stirred for 30 min, followed by extraction with CH_2Cl_2 (30 mL × 3). Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of *n*-hexane and EtOAc (1:3) gave **1a** (260 mg, 90%): mp 122–124°C (EtOH); ^{1}H NMR ($CDCl_3$, 300 MHz): 2.13 (*s*, 3H, CCH_3) 2.29 (*s*, 6H, CH_3CO_2Ar), 3.65 (*m*, 4H, OCH_2), 3.78 (*m*, 4H, OCH_2), 4.12 (*m*, 4H, $ArOCH_2$), 6.68 (*m*, 2H, ArH), 6.82 (*d*, J = 8.67 Hz, 1H, ArH), 6.88–7.10 (*m*, 13H, ArH), 7.26–7.61 (*m*, 3H, ArH); IR (KBr): 3064, 2936, 1752, 1580, 1497, 1438, 1366, 1203 cm^{-1}; MS (ESI) m/z 759 ($[M+Na]^+$). Anal. calcd for $C_{42}H_{40}O_8S_2$: C, 68.48; H, 5.47; S, 8.70. Found: C, 68.19; H, 5.45; S, 8.80.

2,3,20,21-Dibenzo-5,6-[3-{1,1-(di-4-hydroxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16,19-pentaoxacycloheneicosa-2,5,20-triene (8b)

From the reaction of **7** (1.01 g, 1.87 mmol) with the tetraethylene glycol ditosylate (940 mg, 1.87 mmol) in the presence of KOH (530 mg, 9.37 mmol) in DMF (80 mL) at 120–130°C for 5 h was isolated **8b** (590 mg, 45%): mp 194–196°C (EtOAc-*n*-hexane); ^{1}H-NMR (DMSO-d_6, 300 MHz): 1.94 (*s*, 3H, CCH_3), 3.64 (*m*, 12H, OCH_2), 4.06 (*m*, 4H, $ArOCH_2$), 6.60–7.15 (*m*, 18H, ArH), 7.30 (*m*, 1H, ArH), 9.24 (*s*, 2H, OH); IR (neat): 3384, 3280, 2920, 1585, 1507, 1437 cm^{-1}. Anal. calcd for $C_{40}H_{40}O_7S_2$: C, 68.94; H, 5.79; S, 9.20. Found: C, 68.71; H, 5.77; S, 9.21.

2,3,20,21-Dibenzo-5,6-[3-{1,1-(di-4-acetoxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16,19-pentaoxacycloheneicosa-2,5,20-triene (1b)

From the reaction of **8b** (240 mg, 0.34 mmol) with acetyl chloride (80 mg, 1.02 mmol) in the presence of triethylamine (103 mg, 1.02 mmol) in CH_2Cl_2 (20 mL) for 30 min was isolated **1b** (260 mg, 96%): mp 66–68°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.05 (*s*, 3H, CCH_3), 2.29 (*s*, 6H, CH_3CO_2Ar), 3.78 (*m*, 12H, OCH_2), 414 (*m*, 4H, $ArOCH_2$), 6.77 (*d*, J = 8.13 Hz, 1H, ArH), 6.87–7.09 (*m*, 16H, ArH), 7.27 (*m*, 2H, ArH); IR (KBr): 3040, 2912, 2856, 1749, 1571, 1491, 1470, 1437, 1358, 1192 cm^{-1}; MS (ESI) m/z 803 ($[M+Na]^+$). Anal. calcd for $C_{44}H_{44}O_9S_2$: C, 67.67; H, 5.68; S, 8.21. Found: C, 67.49; H, 5.63; S, 8.12.

2,3,23,24-Dibenzo-5,6-[3-{1,1-(di-4-hydroxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16,19,22-hexaoxacyclotetracosa-2,5,23-triene (8c)

From the reaction of **7** (2.05 mg, 3.81 mmol) with pentaethylene glycol ditosylate (2.09 g, 3.81 mmol) in the presence of KOH (1.07 g, 19.1 mmol) in DMF (150 mL) was isolated **8c** (770 mg, 31%): mp 78–80°C (EtOAc–*n*-hexane); ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.79 (*s*, 3H, CCH_3), 3.46–3.56 (*m*, 16H, OCH_2), 3.90 (*m*, 4H, ArOCH_2), 4.75 (*s*, 2H, OH) 6.43 (*d*, *J*=6.65 Hz, 4H, ArH), 6.55 (*m*, 2H, ArH), 6.64 (*d*, *J*=6.85 Hz, 4H, ArH), 6.73 (*m*, 3H, ArH), 6.80 (*m*, 4H, ArH), 7.02 (*m*, 2H, ArH); IR (neat): 3312, 2936, 1585, 1504, 1475, 1438, 1384, 1248 cm^{-1}. Anal. calcd for $C_{42}H_{44}O_8S_2$: C, 68.09; H, 5.99; S, 8.66. Found: C, 67.97; H, 5.91; S, 8.65.

2,3,23,24-Dibenzo-5,6-[3-{1,1-(di-4-acetoxyphenyl)ethyl}]benzo-1,4-dithia-7,10,13,16,19,22-hexaoxacyclotetracosa-2,5,23-triene (1c)

From the reaction of **8c** (880 mg, 1.18 mmol) with acetyl chloride (279 mg, 3.55 mmol) in the presence of triethylamine (359 mg, 3.55 mmol) in CH_2Cl_2) (20 mL) gave **1c** (900 mg, 91%): mp 56–58°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.05 (*s*, 3H, CCH_3), 2.28 (*s*, 6H, CH_3CO_2Ar), 3.61–3.78 (*m*, 16H, OCH_2), 4.12 (*m*, 4H, ArOCH_2), 6.70–7.25 (*m*, 19H, ArH); IR (KBr): 3040, 2912, 2856, 1749, 1568, 1493, 1437, 1360, 1274, 1194 cm^{-1}; MS (ESI) m/z 848 ($[M+Na]^+$). Anal. calcd for $C_{46}H_{48}O_{10}S_2$: C, 66.97; H, 5.86; S, 7.77. Found: C, 66.75; H, 5.83; S, 7.71.

1,1-Bis[4-methanesulfatophenyl]-1-[3-{2-(2-methanesulfatophenylthio)phenylthio}-4-methanesulfatophenyl]ethane (9)

To a solution of **7** (60 mg, 0.11 mmol) and TEA (68 mg, 0.67 mmol) in CH_2Cl_2 (20 mL) was added methanesulfonyl chloride (77 mg, 0.67 mmol) dropwise, which was stirred for 1 h at room temperature. Water (30 mL) was added to the mixture, which was extracted with CH_2Cl_2 (30 mL × 3). The extracts were dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of $CHCl_3$ and MeOH (20:1) gave **9** (80 mg, 84%): mp 72–73°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.01 (*s*, 3H, CCH_3), 3.07 (*s*, 3H, CH_3SO_2), 3.08 (*s*, 6H, CH_3SO_2), 3.10 (*s*, 3H, CH_3SO_2), 6.57–7.55 (*m*, 19H, ArH); IR (neat): 2928, 1576, 1489, 1440, 1361, 1152 cm^{-1}. Anal. calcd for $C_{36}H_{34}O_{12}S_6$: C, 50.81; H, 4.03; S, 22.61. Found: C, 50.77; H, 4.01; S, 22.57.

2,3,20,21-Dibenzo-5,6-[3-{1,1-(di-4-methansulfatophenyl)ethyl}]benzo-1,4-dithia-7,10,13,16,19-pentaoxacycloheneicosa-2,5,20-triene (10)

To a solution of **8b** (70 mg, 0.10 mmol) and TEA (31 mg, 0.30 mmol) in CH_2Cl_2 (20 mL) was added methanesulfonyl chloride (34 mg, 0.30 mmol) dropwise. The mixture was stirred for 2 h and then worked up as for the preparation of **9** to give **10** (80 mg, 93%): mp 88–89°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.10 (*s*, 3H, CCH_3), 3.16 (*s*, 6H, CH_3SO_2), 3.78–3.83 (*m*, 12H, OCH_2), 4.14–4.16 (*m*, 4H, ArOCH_2), 6.79–7.29 (*m*, 19H, ArH); IR (neat): 2928, 1576, 1489, 1440, 1361, 1249, 1152 cm^{-1}. Anal. calcd for $C_{42}H_{44}O_{11}S_4$: C, 59.14; H, 5.20; S, 15.04. Found: C, 58.87; H, 5.18; S, 14.94.

1-(4-Anisyl)-1,1-bis[3-{2-(2-methoxyphenylthio)phenylthio}-4-{methoxy}phenyl]ethane (11)

To a solution of **5** (330 mg, 0.34 mmol) in THF (100 mL) under nitrogen atmosphere was added NaOMe, which was prepared *in situ* from NaH (400 mg, 16.7 mmol) and dried MeOH (160 mg, 4.99 mmol). The mixture was stirred for 48 h. Evaporation of the solvent gave a residue, which was chromatographed on a silica gel column

(10 × 3 cm). Elution with a mixture of EtOAc and *n*-hexane (1:3) gave **11** (150 mg, 53%): mp 84–86°C (EtOH); ^{1}H=NMR ($CDCl_3$, 80 MHz): 1.98 (*s*, 3H, CCH_3), 3.65–3.95 (*m*, 15H, OCH_3), 6.58–7.40 (*m*, 26H, ArH); IR (neat): 3056, 2936, 2832, 1606, 1576, 1500, 1478, 1459, 1388, 1290 cm^{-1}. Anal. calcd for $C_{49}H_{44}O_5S_4$: C, 69.97; H, 5.27; S, 15.25. Found: C, 69.87; H, 5.25; S, 15.24.

1-(4-Hydroxyphenyl)-1,1-bis[3-{2-(2-hydroxyphenylthio)phenylthio}-4-{hydroxy}-phenyl]ethane (12)

To a solution of **11** (290 mg, 0.35 mmol) in CH_2Cl_2 (20 mL) under nitrogen atmosphere was added BBr_3 (2.63 g, 10.5 mmol) dropwise. The mixture was stirred for 24 h, followed by addition of water (30 mL), which was additionally stirred for 1 h. The mixture was extracted with CH_2Cl_2 (30 mL × 5). The extracts were dried over $MgSO_4$. Evaporation of the solvent gave an oily residue, which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of $CHCl_3$ and MeOH (20:1) gave **12** (232 mg, 87%): oily liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.03 (*s*, 3H, CCH_3), 6.40 (brs, 5H, OH), 6.64 (*d*, *J* = 8.77 Hz, 2H, ArH), 6.74 (*m*, 4H, ArH), 6.89 (*m*, 8H, ArH), 7.00 (*m*, 5H, ArH), 7.19 (*s*, 3H, ArH), 7.30 (*t*, *J* = 7.25 Hz, 2H, ArH), 7.43 (*dd*, *J* = 7.72, 1.62 Hz, 2H, ArH); IR (neat): 3400, 2976, 1592, 1498, 1179 cm^{-1}; MS (FAB) m/z 770 (M^+, 0.83%), 755 (0.65).

1,1-Bis(4-anisyl)-1-(4-tolyl)ethane (14)

To a mixture of concentrated H_2SO_4 (1.9 mL) and AcOH (1.6 mL) at room temperature was slowly added a solution of a 4-methylacetophenopne (1.01 g, 7.53 mmol) and anisole (1.97 g, 18.2 mmol) in AcOH (4.3 mL). The mixture was stirred for two weeks at room temperature and then poured to an ice-water (100 mL) to precipitate yellow solids which were filtered to give **14**. Recrystallization from EtOH gave white crystals of **14** (510 mg, 20%): mp 144–145°C (EtOH); ^{1}H-NMR ($CDCl_3$, 80 MHz): 2.10 (*s*, 3H, CCH_3), 2.30 (*s*, 3H, ArCH_3), 3.85 (*s*, 6H, OCH_3), 6.60–7.25 (*m*, 12H, ArH); IR (neat): 2952, 2824, 1600, 1496, 1448, 1283, 1246, 1179, 1027 cm^{-1}; MS m/z 332 (M^+, 10.3%), 317 (100). Anal. calcd for $C_{23}H_{24}O_2$: C, 83.10; H, 7.28. Found: C, 83.07; H, 7.27.

5,5′-[5,5′-{(Methyl)(4-tolyl)methylene-2,2′-dimethoxy}phenyl]bis(thianthreniumyl perchlorate) (15)

To a solution of **3** (6.00 g, 19.0 mmol) in dried CH_3CN (100 mL) was added **14** (1.26 g, 3.80 mmol). The mixture was stirred for 5 days at room temperature. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (10 × 3 cm). Elution with *n*-hexane gave thianthrene (1.26 g, 5.83 mmol). Elution with EtOAc gave an unknown mixture (350 mg). Elution with acetonitrile gave **15** (2.56 g, 70%): mp (dec.) > 300°C; ^{1}H-NMR (DMSO-d_6, 300 MHz): 1.83 (*s*, 3H, CCH_3), 2.37 (s, 3H, ArCH_3), 4.02 (*s*, 6H, OCH_3), 5.60 (*s*, 2H, ArH), 6.56 (*d*, *J* = 8.12 Hz, 2H, ArH), 6.98 (*d*, *J* = 8.10 Hz, 2H, ArH), 7.29 (*d*, *J* = 8.80 Hz, 2H, ArH), 7.41 (*d*, *J* = 8.83 Hz, 2H, ArH), 7.65–7.87 (*m*, 12H, ArH), 8.32 (*s*, 2H, ArH), 8.39 (*d*, *J* = 7.68 Hz, 2H, ArH); IR (KBr): 3064, 2698, 1589, 1554, 1483, 1438, 1286, 1259, 1085 cm^{-1}; MS (ESI) m/z 862 ([M-ClO_4]$^+$). Anal. calcd for $C_{47}H_{38}Cl_2O_{10}S_4$: C, 58.68; H, 3.98; S, 13.33. Found: C, 58.43; H, 3.91; S, 13.30.

1,1-Bis[3-{2-(2-methoxyphenylthio)phenylthio}-4-{methoxy}phenyl]-1-(4-tolyl)ethane (16)

To a suspension of NaH (400 mg, 16.6 mmol) in dried THF (50 mL) at room temperature under nitrogen atmosphere was added dried MeOH (270 mg, 8.32 mmol) dropwise. The mixture was stirred for 30 min, followed by addition of **15** (1.12 g, 1.69 mmol) and 2 mL of DMF in one portion, which was heated for 12 h at reflux and

then cooled to room temperature. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (7 × 1.5 cm). Elution with a mixture of EtOAc and *n*-hexane (1:3) gave **16** (1.01 g, 59%): mp 82–84°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.97 (*s*, 3H, CCH_3), 2.26 (*s*, 3H, $ArCH_3$), 3.78 (*s*, 6H, OCH_3), 3.82 (*s*, 6H, OCH_3), 6.72–7.26 (*m*, 26H, ArH); IR (KBr): 2928, 1568, 1472, 1250 cm^{-1}. Anal. calcd for $C_{49}H_{44}O_4S_4$: C, 71.33; H, 5.37; S, 15.54. Found: C, 71.25; H, 5.36; S, 15.52.

1,1-Bis[3,{2-(2-hydroxyphenylthio)phenylthio}-4-{hydroxy}phenyl]-1-(4-tolyl)ethane (17)

To a solution of **16** (880 mg, 1.07 mmol) in CH_2Cl_2 (30 mL) under nitrogen atmosphere added dropwise BBr_3 (1.33 g, 5.33 mmol). The mixture was stirred for 12 h at room temperature and then slowly poured into water (100 mL), which was extracted with CH_2Cl_2 (30 mL × 5). The extracts were dried over $MgSO_4$. Evaporation of the solvent given an oily residue which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of EtOAc and *n*-hexane (1:3) gave **17** (820 mg, 100%); oily liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.14 (*s*, 3H, CCH_3), 2.34 (*s*, 3H, $ArCH_3$) 6.47 (*s*, 2H, OH), 6.50 (*s*, 2H, OH), 6.84 (*m*, 4H, ArH), 6.96–7.03 (*m*, 10H, ArH), 7.07–7.11 (*m*, 6H, ArH), 7.30 (*sd*, J = 2.42 Hz, 2H, ArH), 7.40 (*t*, J = 7.50 Hz, 2H, ArH), 7.53 (*dd*, J = 7.72, 1.67 Hz, 2H, ArH); IR (neat): 3424, 3048, 2968, 1564, 1467, 1182 cm^{-1}; MS m/z 768 (M^+, 38.9%), 753 (45.2), 5.38 (60.7), 523 (100).

1,1-Bis[3,4-(2,3,20,21-dibenzo-1,4-dithia-7,10,13,16,19-pentaoxacycloheneicosa-2,5,20-triene)phenyl]-1-(4-tolyl)ethane (18)

To a mixture of **17** (790 mg, 1.03 mmol) and Cs_2CO_3 (1.34 g, 4.12 mmol) in DMF (100 mL) at room temperature was added a solution of tetraethylene glycol ditosylate (1.09 g, 2.17 mmol) in DMF (50 mL). The mixture was stirred for 5 h at 60–70°C. The cooled reaction mixture was poured into water (300 mL), which was additionally stirred for 2 h. The yellowish white solids formed were filtered. The solids were dissolved in CH_2Cl_2 (200 mL), which was washed with water (50 mL) and then dried over $MgSO_4$. Removal of the solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with EtOAc gave **18** (570 mg, 51%); mp 87–89°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.94 (*s*, 3H, CCH_3), 2.21 (*s*, 3H, $ArCH_3$), 3.72 (*m*, 24H, OCH_2), 4.01 (*m*, 4H, $ArOCH_2$), 4.08 (*m*, 4H, $ArOCH_2$), 6.64 (*d*, J = 9.25 Hz, 2H, ArH), 6.79–7.19 (*m*, 24H, ArH); IR (KBr): 3048, 2856, 1569, 1470, 1436, 1272, 1244 cm^{-1}; MS (ESI) m/z 565 ($[M/2+Na]^+$). Anal. calcd for $C_{61}H_{64}O_{10}S_4$: C, 67.50; H, 5.94; S, 11.82. Found: C, 67.26; H, 5.93; S, 11.79.

5,5′,5″-[5,5′,5″-{(Methyl)methylene-2,2′,2″-trimethoxy}phenyl]tris(thianthreniumyl perchlorate) (19)

To a solution of **3** (6.50 g, 20.6 mmol) in dried CH_3CN (50 mL) at room temperature was added **2** (1.43 g, 4.12 mmol), which was stirred for 5 days. Removal of solvent *in vacuo* gave a residue which was washed with diethyl ether (100 mL × 3), followed by drying *in vacuo*. A solution of **3** (6.20 g, 19.6 mmol) in CH_3CN (50 mL) was transferred to the dried residue. The mixture was additionally stirred for 4 days. Removal of solvent *in vacuo* gave a residue, which was chromatographed on a silica gel column (15 × 1.5 cm). A successive elution with *n*-hexane and EtOAc gave thianthrene and a mixture of **4** and **5**, respectively. Elution with acetone gave yellowish solids **19** (3.60 g, 69%): mp 224–226°C (EtOH); ^{1}H-NMR (DMSO-d_6 300 MHz): 1.66 (*s*, 3H, CCH_3), 4.09 (*s*, 9H, OCH_3), 5.31 (*s*, 3H, ArH), 7.23 (*m*, 6H, ArH), 7.64–7.83 (*m*, 18H, ArH), 8.40 (*d*, J = 7.93 Hz, 6H, ArH); IR (KBr): 3056, 2976, 1589, 1554, 1483, 1442, 1280, 1085, 998, 758 cm^{-1}. Anal. calcd for $C_{59}H_{45}Cl_3O_{15}S_6$: C, 54.82; H, 3.51; S, 14.88. Found: C, 54.76; H, 3.51; S, 14.85.

1,1,1-Tris[4-methoxy-3-{2-(2-methoxyphenylthio)phenylthio}phenyl] ethane (20)

From the reaction mixture obtained from the reaction of **19** (1.50 g, 1.18 mmol) with NaOMe, prepared *in situ* from MeOH (378 mg, 11.8 mmol) and NaH (430 mg, 17.9 mmol), in THF (30 mL) as described for the preparation of **16** was obtained **20** (660 mg, 51%): mp 88–92°C (EtOH); ^{1}H-NMR ($CDCl_3$, 300 MHz): 193 (*s*, 3H, CCH_3), 3.79 (*s*, 9H, OCH_3), 3.85 (*s*, 9H, OCH_3), 6.70 (*d*, J = 8.28 Hz, 3H, ArH), 6.85–7.29 (*m*, 30H, ArH); IR (KBr): 3040, 2928, 2824, 1566, 1472, 1432, 1267, 1250 cm^{-1}. Anal. calcd for $C_{62}H_{54}O_6S_6$: C, 68.48; H, 5.01; S, 17.69. Found: C, 68.57; H, 5.20; S, 17.58.

1,1,1-Tris[4-hydroxy-3-{2-(2-hydroxyphenylthio)phenylthio}phenyl] ethane (21)

From the reaction of **20** (660 mg, 0.61 mmol) with BBr_3 (950 ml, 3.81 mmol) in CH_2Cl_2 as described for the preparation of **17** was obtained **21** (550 mg, 90%): oily liquid; ^{1}H-NMR ($CDCl_3$, 300 MHz): 2.15 (*s*, 3H, CCH_3), 6.49 (*s*, 6H, OH), 6.83 (*m*, 6H, ArH), 6.99 (*m*, 12H, ArH), 7.09 (*m*, 6H, ArH), 7.29 (*m*, 2H, ArH), 7.40 (*t*, J = 7.65 Hz, 3H, ArH), 7.53 (*dd*, J = 7.68, 1.46 Hz, 3H, ArH); IR (neat): 3416, 3048, 2968, 1563, 1467 cm^{-1}; MS (FAB): 1002 ([M]$^+$, 3.16%), 987 (5.55), 6.77 (8.61).

1,1,1-Tri[3,4-(2,3,20,21-dibenzo-1,4-dithia-7,10,13,16,19-pentaoxacycloheneicosa-2,5,20-triene)phenyl]ethane (22)

From the reaction of **21** (540 mg, 540 mmol) with tetraethylene glycol ditosylate (900 mg, 1.79 mmol) in the presence of Cs_2CO_3 (1.06 g, 3.25 mmol) in DMF (200 mL) as described for the preparation of **18** was obtained crude **22**, which was chromatographed on a silica gel column (15 × 1.5 cm). Elution with a mixture of three solvents ($CHCl_3$: EtOAc : MeOH = 15:5:1) gave **22** (190 mg, 24%): mp 94–96°C; ^{1}H-NMR ($CDCl_3$, 300 MHz): 1.97 (*s*, 3H, CCH_3), 3.81 (*m*, 36H, OCH_2), 4.08 (*m*, 6H, $ArOCH_2$), 4.16 (*m*, 6H, $ArOCH_2$), 6.67 (*d*, J = 8.19 Hz, 3H, ArH), 6.86–7.28 (*m*, 30H, ArH); IR (KBr): 3040, 2912, 2864, 1571, 1470, 1438, 1270, 1248, 1125 cm^{-1}; MS (ESI) m/z 1500 ([M + Na]$^+$), 762 ([M/2 + Na]$^+$). Anal. calcd for $C_{80}H_{84}O_{15}S_6$: C, 65.02; H, 5.73; S, 13.02. Found: C, 64.86; H, 5, 71; S, 12.94.

Solvent Extraction

The extraction of metal ions from the aqueous solution into chloroform was performed in capped test tubes. For blank rest. For blank rest, biphasic mixtures (the volumes of water and chloroform are 2 mL each) was stirred vigorously for 1 min and then kept at 25°C ± 1°C for 12 h. The amount of picrate anion in the aqueous phase was determined by UV-VIS spectroscopy measured at 354 nm. Likewise, the amount of picrate anion remained in the aqueous phase after being extracted by the host molecules in the organic phase was determined by the same method. The extractability was calculated according to Eq. (1). All experiments were carried out in duplicate or triplicate and the respective results were averaged. The results are summarized in Table I.

Transport through a Liquid Membrane

The transport experiments were performed in a U-tube glass cell (1.5 cm, i.d) at 25°C ± 1°C. Chloroform (10 mL) containing ionophore (1×10^{-3} M) was placed in the base of U-tube. For noncompetitive transport, deionized water (5 mL) containing each picrate (5×10^{-3} M) and deionized water (5 mL) were placed in each tube arm. The membrane phase was constantly stirred with a stirring bar (1000 rpm) on the bottom of the cell. After 40 h, the concentration of the ions in the aqueous receiving phase were

determined by inductively Coupled Plasma Atomic Absorption Spectroscopy. For competitive transport, deionized water (5 mL) containing four picrate (2×10^{-3} M) was employed under the same conditions as for noncompetitive transport. The results from non- and competitive transports are summarized in Tables II and III, respectively.

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