Synthesis of 2-(arylthio)-3'-(alkyl- or dialkylamino)diphenyl sulfides via 5-arylthianthrenium perchlorates and their complexations with silver(I) and lead(II) ions

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Dedicated to Professor Henry J. Shine on the occasion of his 80th birthday

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Abstract

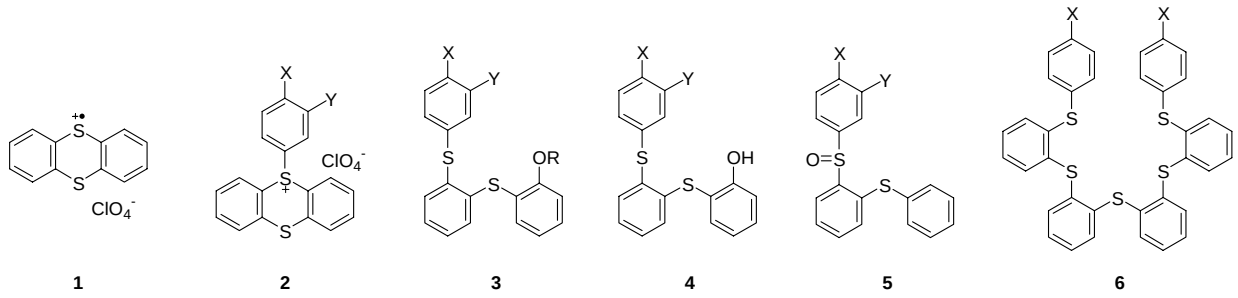
Treatment of 5-arylthianthrenium perchlorates **2** with secondary alkylamines in the presence of LDA in THF at reflux gave 2-(arylthio)-3'-(dialkylamino)diphenyl sulfides **7** as major products along with 2-(arylthio)-2'-(dialkylamino)diphenyl sulfides **8** and thianthrene. The latter two compounds were formed depending on the structures of amines employed and the concentrations of LDA. It has been found that the methoxy groups of **7e**, **7g**, and **7h** were displaced by amide ions in the presence of excess amounts of LDA to give the corresponding 2-(4-dialkylaminophenylthio)-3'-(dialkylamino)diphenyl sulfides (**14a-c**). The reactions with aza-15-crown-5, aza-18-crown-6, and 7, 16-diaza-18-crown-6 gave analogous products via a benzyne intermediate.

The affinity of selected metal cations for compounds **7a**, **7e-f**, **7h**, **7j**, **7m**, **10**, **13a**, and **18a** was examined by an extraction method. The dialkylamino groups of **7a**, **7e**, **7f**, and **7h** increased somewhat the extractive abilities of Ag^+ ion (14 - 28%) compared with that of **10** (8%), whereas compound **13a** having a diisopropylamino group showed low (9%) and high (67%) extractive abilities toward Ag^+ and Pb^{2+} ions, respectively. Compounds **7j** and **7m** having an aza-18-crown-6 moiety showed 67% and 66% extractive abilities toward Pb^{2+} but 40% and 24% extractive abilities towards Ag^+ ions, respectively. However, compound **18a** with two identical lariats showed high (86%) and low (12%) extractive abilities toward Ag^+ and Pb^{2+} ions, respectively.

Keywords: 2-(Arylthio)-3'-(dialkylamino)diphenyl sulfides, 2-(arylthio)-2'-(dialkylamino)-diphenyl sulfides, 2-(4-dialkylaminophenylthio)-3'-(dialkylamino)diphenyl sulfides

Introduction

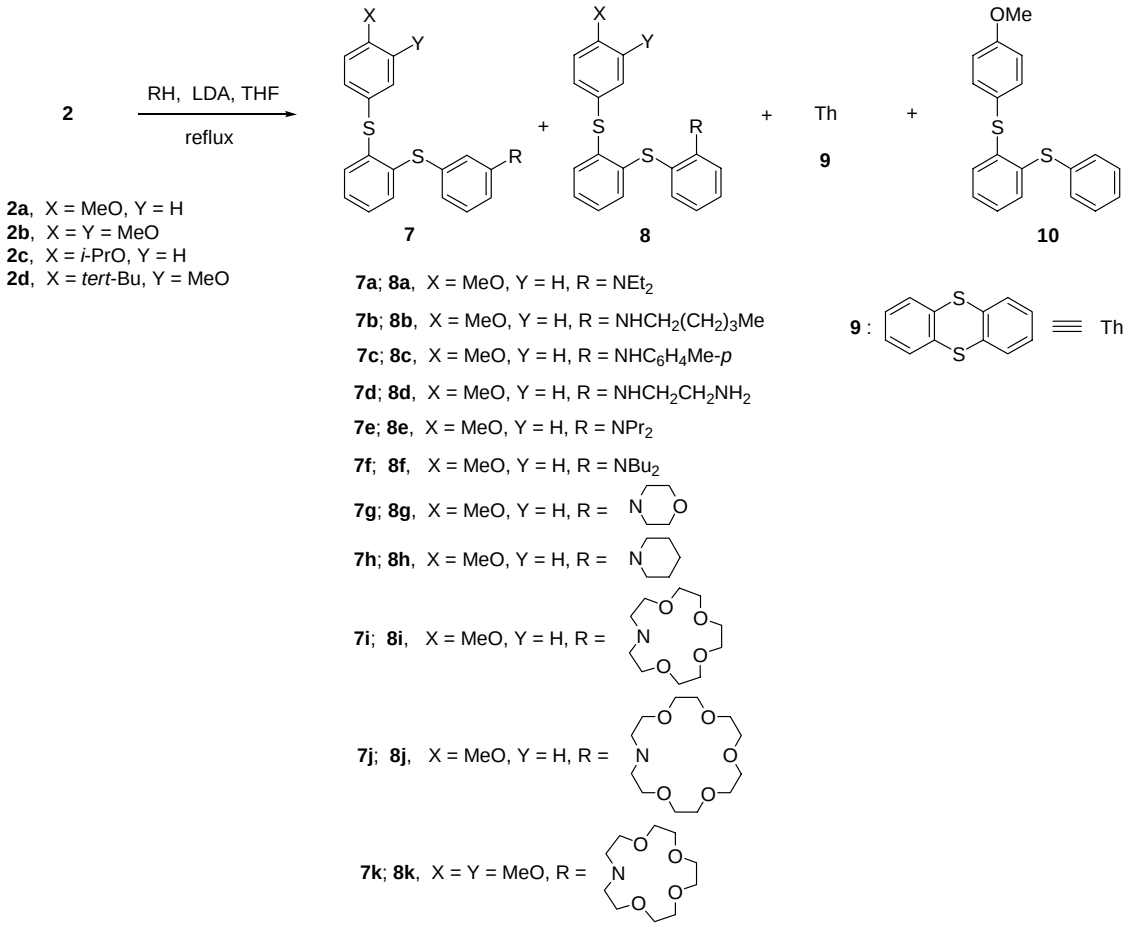
Thianthrene cation radical perchlorate (**1**) is a crystalline solid which is stable at room temperature under anhydrous conditions. Its physical and chemical properties and reactivity have been extensively studied.[1] It reacts with aromatics having an electron-donating group in CH_3CN at room temperature to give 5-arylthianthrenium perchlorates **2**.[2] It has been found that compounds **2** are useful precursors for the synthesis of some sulfur-containing organic compounds. For example, compound **2a** was converted to 2-alkoxy-2'-(arylthio)diphenyl sulfides **3** on heating with alkoxide in alcohol at reflux.[3] Dealkylation of **3** to give 2-(arylthio)-2'-hydroxydiphenyl sulfides **4** (66 - 88%) was achieved on heating with 48% HBr in HOAc at 110 ° C[4] or stirring with BBr_3 in CH_2Cl_2 at room temperature.[5] Treatment of **2** with *tert*-BuOK in DMSO at room temperature gave 2-(arylsulfinyl)diphenyl sulfides **5**,[6] which are regioselective oxidation products of 2-(arylthio)diphenyl sulfides. Interestingly, heating a mixture of **2** and $NaSH{\cdot}xH_2O$ in either PhH/H_2O (1 : 1, v/v) or THF/H_2O (10 : 1, v/v) at reflux resulted in the formation of 2,2'-bis[2-(arylthio)phenylthio]diphenyl sulfides **6**.[7]



1 **2** **3** **4** **5** **6**

Recently, we reported that compounds **2** (X = MeO, Y = H) reacted with diethylamine in the presence of LDA in THF at reflux to give 2-(4-anisylthio)-3'-(diethylamino)diphenyl sulfide (**7a**) (57%) and 2-(4-anisylthio)-2'-(diethylamino)diphenyl sulfide (**8a**) (11%) together with thianthrene (**9**) (8%)[8] (Scheme 1).

Compound **7a** was proven to be formed via a benzyne intermediate. This result suggests that compound **2** can be utilized as a new substituted benzyne precursor. To study the scope of the reaction, the reactions with diverse primary and secondary alkylamines were investigated. In addition, complexations of **7a**, **7e** (X = MeO, Y = H, R = Pr_2N), **7f** (X = MeO, Y = H, R = Bu_2N), **7h** (X = MeO, Y = H, R = ), **7j** (X = MeO, Y = H, R = 1,4,7,10,13-pentaoxa-16-azacyclooctadec-16-yl), **7m** (X = *i*-PrO, Y = H, R = 1,4,7,10,13-pentaoxa-16-azacyclooctadec-16-yl), **10** and **13a** (X = MeO, Y = H, R = $(i\text{-Pr})_2N$) with selected metal cations were studied in order to understand the effects of 2-(arylthio)phenylthio group as a lariat. The results are described herein.

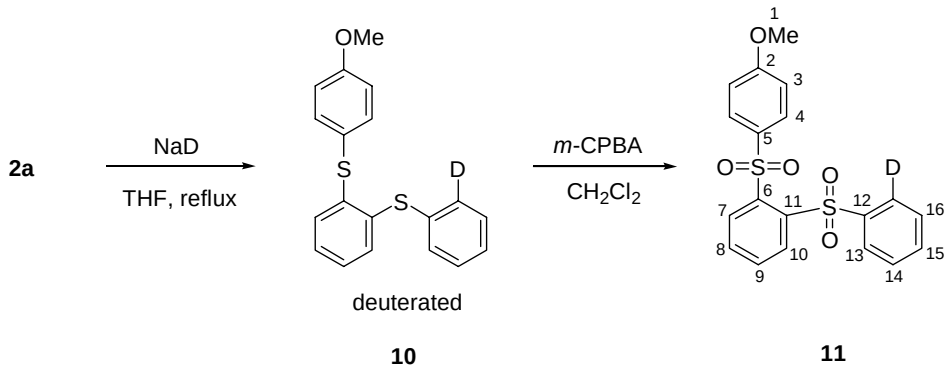


Scheme 1

Results and Discussion

To begin with, treatment of **2a** with a primary alkylamine such as pentylamine (2.3 equiv.) in the presence of NaH (5.3 equiv.) for 3 h in THF at reflux gave 2-(4-methoxyphenylthio)-3'-(pentylamino)diphenyl sulfide (**7b**) (X = MeO, Y = H, R = pentylNH) (21%), 2-(4-methoxyphenylthio)diphenyl sulfide (**10**) (31%), and **9** (18%) (entry 1, Table 1). No **8b** (X = MeO, Y = H, R = pentylNH) was obtained. On the other hand, the same reaction was conducted by adding LDA (2 M, hexane) in place of NaH. LDA (0.3 mL, 0.6 mmol) was added six times at 40 min intervals during the reaction since LDA was expected to be deteriorated at reflux temperature. From the reaction were obtained **7b** and **9** in 26 and 16% yields, respectively (entry 2, Table 1). No **8b** was obtained. In order to identify the bonding position of the incoming H^- ion leading to **10**, **2a** was treated with NaD in place of NaH under the same foregoing conditions to give deuterated **10** in 63% yield (Scheme 2). However, the assignment of each of the aromatic protons of deuterated **10** on the basis of the ^{1}H NMR spectrum was unsuccessful simply because

of poor resolution. Accordingly, the deuterated **10** was oxidized with *m*-CPBA to give disulfone **11**.



Scheme 2

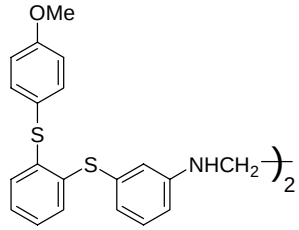
The 2D NMR spectrum of **11** showed a multiplet at 7.94 ppm, assigned to two H4 protons and one H13 proton, whose intensity was compared with that obtained from the same compound not possessing a deuterium atom. Although we are aware of the deuterium atomic bonding position, further study is necessary to delineate the mechanism for the formation of **10**. Similar reaction of **2a** with *p*-toluidine (2.0 equiv.) and NaH (2.3 equiv.) gave **7c** (X = MeO, Y = H, R = *p*-MeC_6H_4NH) and **9** in 28 and 41% yields, respectively (entry 3). No **10** was detected. Arylamine is more acidic than alkylamine which may account for decreased availability of NaH. No **10** was detected in both reactions. Interestingly, the reaction of **2a** with ethylenediamine (4 equiv.) and LDA (0.3 mL x 4) gave **7d** (X = MeO, Y = H, R = $HNCH_2CH_2NH_2$) in 45% yield (entry 4), whereas *N*,*N*-disubstituted ethylenediamine derivative **12** was obtained in 72% yield when **2a** (5 equiv.) was treated with ethylenediamine and LDA (0.3 mL x 8) (entry 5). Since a large quantity of **9** was obtained from the reaction with primary arylamine and NaH (entry 3), coupled with a relatively high yield of **7a** from the reaction with diethylamine and LDA (entry 6), we decided to study the reactions of **2** with secondary alkylamines in the presence of LDA. The yields of **7**, **8**, and **9** are summarized in Table 1.

Table 1. Quantities of **2** and amines, and yields of **7**, **8**, and **9**

entry	compound	mmol	RH[b]	mmol	compd	yield[a] (%)		
						7	**8**	**9**
1	**2a**	0.71	$PentylNH_2$[c]	1.64	**b**	21	0	18
2	**2a**	0.47	$PentylNH_2$	4.02	**b**	26	0	16
3	**2a**	0.47	$MeC_6H_4NH_2$[c]	0.95	**c**	28	0	41
4	**2a**	0.47	$H_2N(CH_2)_2NH_2$[e]	1.89	**d**	45	0	0
5	**2a**	2.32	$H_2N(CH_2)_2NH_2$[g]	0.46			[m]	
6	**2a**	1.42	Et_2NH[e, h]	8.20	**a**[8]	57	11	9

7	**2a**	0.47	Et_2NH[d, e]	6.84	**a**	51	19	18
8	**2a**	0.47	Pr_2NH[g]	1.89			[n]	
9	**2a**	0.47	Pr_2NH[d, e]	excess	**e**	55	0	0
10	**2a**	0.54	Bu_2NH[e]	excess	**f**	29	2	25
11	**2a**	0.47	 [d, e]	1.18	**g**	74	15	0
12	**2a**	0.47	 [d, g]	1.18			[o]	
13	**2a**	0.47	 [d, e]	3.52	**h**	62	14	9
14	**2a**	0.47	 [d, g]	excess			[p]	
15	**2a**	2.32	 [f, i]	0.46			[q]	
16	**2a**	1.68	1-aza-15-crown-5[f, h]	0.56	**i**	33	0	sm[t]
17	**2a**	1.20	1-aza-18-crown-6[f, h]	0.40	**j**	82	0	sm
18	**2a**	2.29	1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane[f, h]	0.38			[r]	
19	**2b**	1.17	1-aza-15-crown-5[f, j]	0.57	**k**	40		
20	**2b**	2.22	1-aza-18-crown-6[f, j]	0.44	**l**	56	0	sm
21	**2b**	3.32	1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane[f, j]	0.42			[s]	
22	**2c**	2.44	1-aza-18-crown-6[f, k]	0.41	**m**	47	0	sm
23	**2d**	1.96	1-aza-18-crown-6[f, l]	0.39	**n**	41	0	sm

[a] Isolated yields. [b] For the reactions (entries 1 - 4 and 6 - 14), excess molar amounts of amines were used compared with those of **2**. For the remainder (entries 5 and 15 - 23), yields of products were calculated based on the amounts of amines employed. [c] LDA (2 M, hexane) was used as a base except for two cases (entries 1 and 3) where NaH was employed. Each time 0.3 mL of LDA was added at 40 min intervals during the reaction. The number of additions is specified each case. [d] Dried amines were used. Otherwise, purchased amines were used. [e] Number of additions of LDA: 2. [f] Number of additions of LDA: 6. [g] Number of additions of LDA: 8. [h] Additionally a spot corresponding to **13a** was observed on TLC (silica-gel, EtOAc/hexane = 1 : 3). [i] Additionally **13a** was obtained in 27% yield. [j] A spot corresponding to **13b** was observed on TLC. [k] A spot corresponding to **13c** was observed on TLC. [l] A spot corresponding to **13d** was observed on TLC. [m] Compounds **12** and **9** were obtained in 72 and 11% yields, respectively. [n] Compounds **14a**, **15a**, and **9** were obtained in 49, 10, and 15% yields, respectively. [o] Compounds **14b** and **15b** were obtained in 42 and 17% yields, respectively. [p] Compounds **14c** was obtained in 45% yield. [q] Compound **17** was obtained in 71% yield. [r] Compounds **18a** was obtained in 55% yield. [s] Compound **18b** was obtained in 33% yield. [t] sm : small amount. In the cases of entries 15 - 23, a mixtures of small amounts of **9** and unidentifiable materials were obtained.



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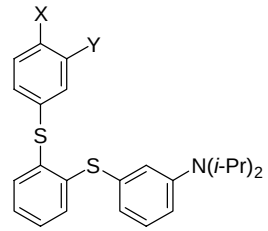
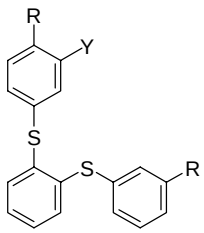


13a, X = MeO, Y = H
13b, X = Y = MeO
13c, X = *i*-PrO, Y = H
13d, X = *tert*-Bu, Y = MeO



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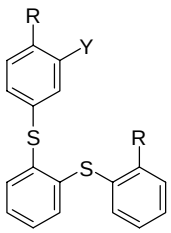
a, R = NPr_2 , Y = H

b, R =  , Y = H

c. R =  , Y = H



15

The structures of compounds **7a-n**, **8a**, **8f-h**, **13a**, **14a-c**, **15a-b**, **17**, **18a-b** were identified on the basis of spectroscopic (^{1}H and ^{13}C NMR, IR, MS) and analytical data. Reactions with dried amines (i.e., diethylamine (entry 7) and dipropylamine (entry 9)) were compared with reactions where the same amines had not been previously dried. When purchased Et_2NH (5.7 equiv.) and LDA (0.3 mL x 2) were employed, **7a**, **8a**, and **9** were obtained (entry 6). In addition, a spot corresponding to **13a** was observed on TLC (EtOAc : hexane = 1 : 3, R_f = 0.45). By employing a dried excess amount of Et_2NH (15 equiv.) and the same amount of LDA, only **7a**, **8a**, and **9** were obtained in 51, 19, and 18% yields, respectively (entry 7). Yields of **7a**, **8a**, and **9** seemed to be independent of the dryness of Et_2NH. In addition, no spot corresponding to **13a** was observed from the latter reaction presumably due to the low concentrations of diisopropylamide ion in the presence of excess Et_2NH.

For the reactions with an excess amount of dried Pr_2NH and LDA (0.3 mL x 2) (entry 9), **7e** was obtained in 55% yield, whereas the reaction with purchased Pr_2NH (4 equiv.) and LDA (0.3 mL x 8) gave **14a**, **15a**, and **9** in 49, 10, and 15% yields (entry 8) instead of **7e** and **8e**. This result indicates that the reactions depend strongly on the concentration of LDA rather than the dryness of purchased amines. The formation of **14a** and **15a** may be achieved via a nucleophilic displacement of the methoxy groups of **7e** and **8e** by dipropylamide ion. The displacement of the methoxy group in preference to the phenylthio group indicates that the first step corresponding to a nucleophilic attack of an amide ion is a rate determining step.[9] However, the electronic (for **7e** and **8e**) and steric (for **8e**) effects of dipropyl groups of **7e** and **8e** cannot be ruled out.

The importance of the concentrations of LDA was also observed from the reaction with dried morpholine (entries 11 and 12) and dried piperidine (entries 13 and 14). That is, 0.3 mL of LDA was added twice (entry 11) and eight times (entry 12) to the same amounts of a mixture of **2a** and morpholine, respectively. After the reaction mixture was allowed to proceed for 6 h, the former reaction gave **7g** and **8g** in 74 and 15% yields, respectively, whereas the latter reaction gave **14b** and **15b** in 42 and 17% yields, respectively. The structure of **14b** was confirmed by X-ray crystallography (Figure 1).

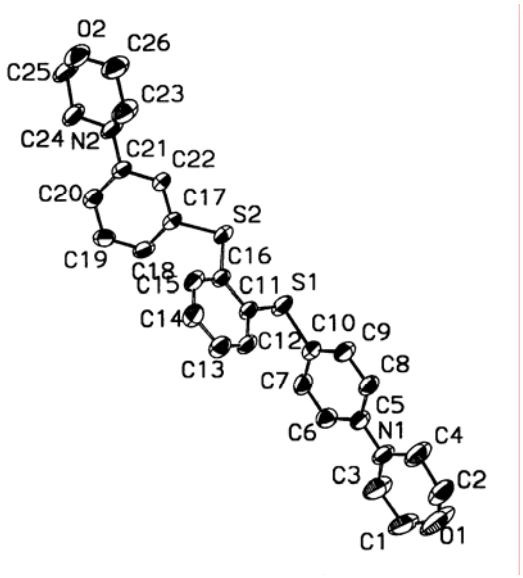
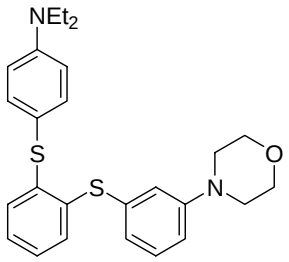


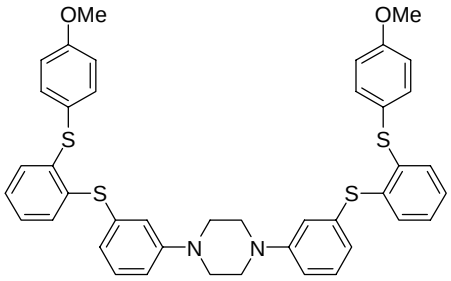
Figure 1. ORTEP drawing of **14b**.

The formation of **14b** from **7g** was confirmed by an independent study in which treatment of **7g** (144 mg, 0.35 mmol) with dried morpholine (150 mg, 1.72 mmol) and LDA (0.3 mL x 6) under the same foregoing conditions gave **14b** in 92% yield. However, the same reaction of **7g** with Et_2NH did not give the corresponding substitution product **16**. The failure to form **16** may be due to the low boiling point of Et_2NH. Similarly, the reaction with piperidine (7.5 equiv.) and LDA (0.3 mL x 2) gave **7h**, **8h**, and **9** in 62, 14, and 9% yields, respectively (entry 13), whereas the reaction with an excess amount of piperidine and LDA (0.3 mL x 8) resulted in the formation of **14c** in 45%. No **7h** and **8h** were obtained.



16

The reaction with piperazine (0.2 molar equiv.) and LDA (0.3 mL x 6) gave *N*,*N'*-bis[3-{2-(4-methoxyphenylthio)phenylthio}phenyl]piperazine (**17**) and **13a** in 71 and 27% yields, respectively, along with a small amount of **9** containing some unidentifiable mixtures (entry 15).



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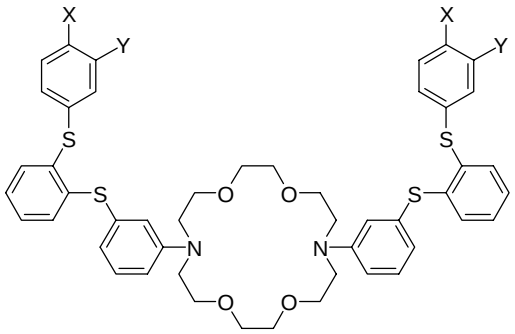


18a, X = MeO, Y = H
18b, X = Y = MeO

The reactions of azacrown ethers, i.e., aza-15-crown-5 (1,4,7,10-tetraoxa-13-azacyclopentadecane) and aza-18-crown-6 (1,4,7,10,13-pentaoxa-16-azacyclooctadecane), with **2a** (3 equiv.) (entries 16 - 17) and LDA (0.3 mL x 6) gave the corresponding *N*-[3-{2-(4-methoxyphenylthio)phenylthio}phenyl]-1-azacrown ethers (**7i-j**) together with a small amount of **13a** and **9**. In the meantime, the same reaction of 7,16-diaza-18-crown-6 (1,4,10,13-tetraoxa-7,16-diazacyclooctadecane) with **2a** (6 equiv.) under the same conditions gave **18a** in 55% yield (entry 18). Similar reactions of **2b** (X = Y = MeO) (entries 19 - 20), **2c** (X = *i*-PrO, Y = H) (entry 22), and **2d** (X = *tert*-Bu, Y = MeO) (entry 23) in the presence of LDA (0.3 mL x 6) under the same foregoing conditions gave the corresponding **7k-l** and **7m-n** together with **13b** (X = Y = MeO), **13c** (X = *i*-PrO, Y = H), and **13d** (X = *tert*-Bu, Y = MeO), respectively, and a small amount of **9**. Treatment of 7,16-diaza-18-crown-6 with **2b** (7.9 equiv.) under the same conditions gave **18b** in 33% yield (entry 21).

Complexations of some prepared sulfur-containing compounds.

(a) Extractive ability

The affinity of selected metal cations to compounds **7a**, **7e-f**, **7h**, **7j**, **7m**, **10**, **13a**, and **18a** was examined by mixing a deionized aqueous solution of a metal picrate (5 x 10^{-3} M, 2 mL), prepared by a reported procedure,[10] with each of the host compounds in $CHCl_3$ (1 x 10^{-3} M, 2 mL). The mixture was vigorously stirred, followed by maintenance at constant temperature for 12 h. The extractive ability defined in equation 1 was calculated, where the subtraction of the picrate transferred into the plain $CHCl_3$ from the initial concentration of picrate in the aqueous phase is the $[M_{aq}]$ value, and $[M_t]$ is the concentration of picrate in the aqueous phase after extraction. $[H_o]$ is the concentration of the host molecule. The results are tabulated in Table 2.

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

Table 2. Extractive ability of some compounds

compd / metal ion	**10**	**7a**	**7e**	**7f**	**7h**	**7j**	**7m**	**18a**	**13a**

Na^+	0	3	0	0	6	0	0	0	3
K^+	4	1	0	0	4	0	0	0	5
Cs^+	8	3	0	0	8	0	0	0	0
Cu^{2+}	0	9	4	7	10	0	0	3	24
Ag^+	8	28	18	14	28	40	24	86	9
Cd^{2+}	0	4	6	1	3	0	0	1	10
Ba^{2+}	3	1	0	0	3	19	15	0	0
Pb^{2+}	0	18	5	7	19	67	66	12	67

Table 2 shows that the extractive abilities of **10** toward all metal cations employed are essentially zero. In contrast, the extractive abilities of **7a** having a diethylamino group at the meta position toward Ag^+ and Pb^{2+} ions increased somewhat to 28 and 18%, respectively. On the other hand, the extractive abilities of **7e** and **7f** having a dipropyl- and dibutylamino group, respectively, in place of a diethylamino group of **7a** toward the same metal ions decreased to 18 and 5%, respectively, for **7e**, and to 14 and 7%, respectively, for **7f**. The results suggest that the nonbonding electrons on the amino group at the meta position are somehow involved in the complexations with both Ag^+ and Pb^{2+} ions. However, bulky groups such as the dipropyl- and dibutylamino groups are envisaged to reduce the efficiency of the complexations, presumably due to the steric hindrance. Compound **7h**, having a piperidine moiety at the same meta position showed almost the same extractive abilities as those of **7a** toward Ag^+ and Pb^{2+} ions. This may be ascribed to the similar electronic and steric effects of the piperidine ring and diethylamino group. In this regard, it is necessary to explain the observation in which compound **13a**, having a diisopropylamino group at the same meta position, showed a very low extractive ability (9%) toward Ag^+ ion and a relatively high extractive ability (67%) toward Pb^{2+} ion. One might explain the different tendencies in the extractive ability of **13a** toward Ag^+ ion and Pb^{2+} ions by presuming the involvement of two molecules of **13a** in producing a cavity for complexing metal ions. The cavity may be suitable for accommodation of the smaller Pb^{2+} ions (ionic radius = 1.20 Å) compared with Ag^+ ions (ionic radius = 1.26 Å).[11]

Figure 2 shows molecular mechanics-calculated conformations ($MN2^+$ force field, MC/SD conformational search)[12] of (a) **13a** (parallel) – Pb^{2+}, (b) **13a** (parallel, T-shaped[13]) – Pb^{2+}, and (c) **13a** (anti-parallel) – Pb^{2+} picrate complexes.

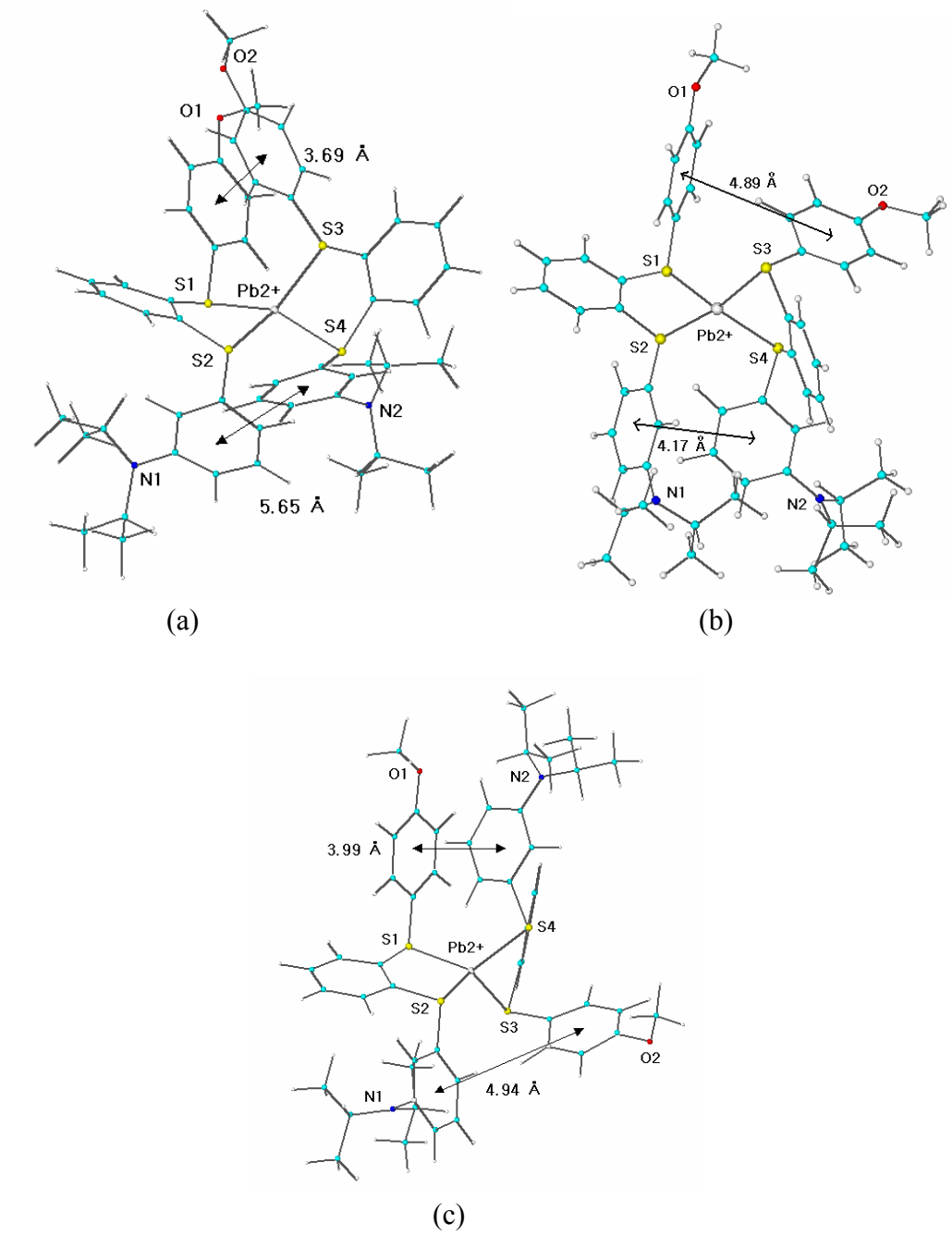


Figure 2. Molecular mechanics-calculated conformations of (a) **13a** (parallel) – Pb^{2+}, (b) **13a** (parallel, T-shaped) – Pb^{2+}, and (c) **13a** (anti-parallel) - Pb^{2+} picrate complexes.

The non-bonded distances between the middle of the methoxyphenyl groups bonded to S1 and S3 atoms, and two diisopropylaminophenyl groups bonded to S2 and S4 atoms of the **13a** (parallel) – Pb^{2+} and the **13a** (parallel, T-shaped) – Pb^{2+} picrate complexes are calculated to be 3.69 and 5.65 Å, and 4.89 and 4.17 Å, respectively. Similarly, the non-bonded distances between two phenyl groups bonded to S1 and S4, and S2 and S3 atoms of the **13a** (anti-parallel) - Pb^{2+} are

3.99 and 4.94 Å , respectively. The distances over 4 Å are a little greater for π- π stacking interactions.[14] It shows that a Pb^{2+} ion interacts with four sulfur atoms whose geometry resembles a crushed tetrahedral (refer to the supporting information (SI) for non-bonded distance and bond angle). The interaction energies between the HOMO of **13a** and the LUMO of Pb^{2+} ion (refer to the SI for the energies of the HOMO and the LUMO),[15] and the thermodynamic energies of the complexes are summarized in Table 3.

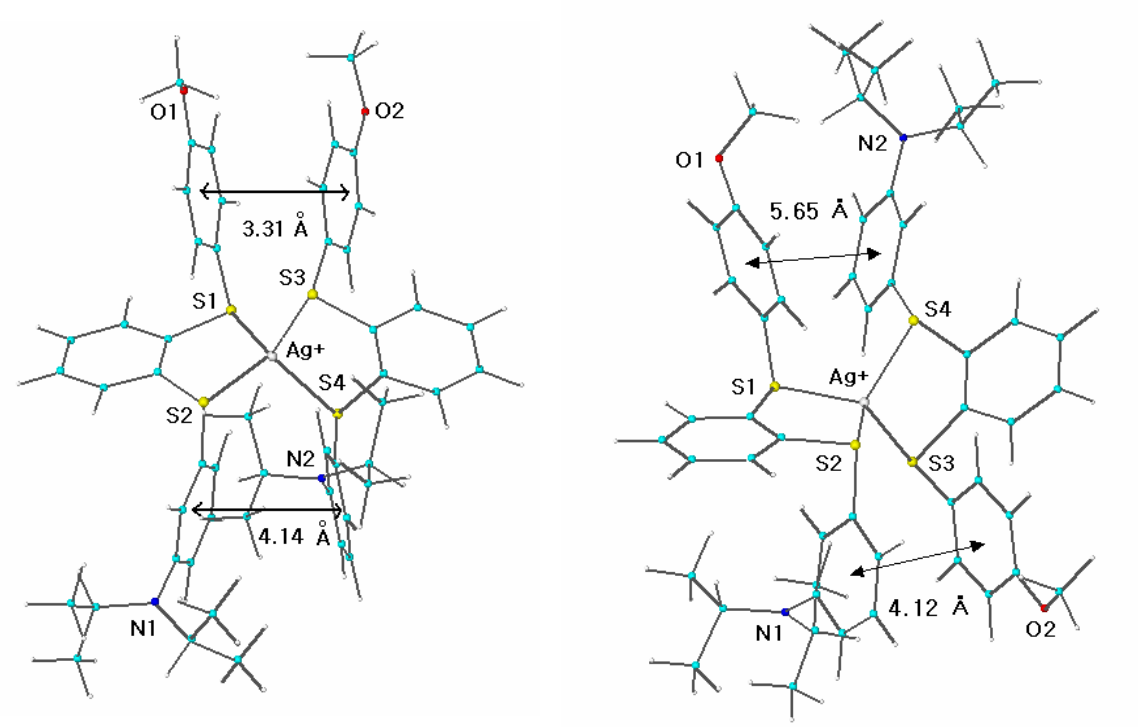
Table 3. The energy differences between the HOMO of **13a** and the LUMO of metal cations (Pb^{2+}, Ag^{+}) and the thermodynamic energies of **13a** – metal cation complexes at 25 ^{o}C

complex / energy	**13a** (P) – Pb^{2+}	**13a** (P, T) – Pb^{2+}	**13a** (A P) - Pb^{2+}	**13a** (P) – Ag^{+}	**13a** (A P) - Ag^{+}
ΔE (HOMO – LUMO) eV	9.332 (α & β)	1.903 (α) 1.879 (β)	8.687 (α & β)	12.272 (α) 12.979 (β)	11.024 (α) 11.669 (β)
E (thermodynamic) kcal/mol	1,053.17	42.18	1,071.23	1,269.92	1,284.25

P: parallel; A P: anti-parallel; T: T-shaped; α : α -spin; β: β –spin.

The data show that the **13a** (parallel, T-shaped) – Pb^{2+} picrate complex has a lower thermodynamic energy compared with other complexes by 1011 to 1029 kcal/mol. Furthermore, the smallest HOMO –LUMO interaction energy (1.9 eV) is involved in the formation of the complex. Consequently, not only the thermodynamic stability of the complex but also the HOMO – LUMO interaction energy are envisaged to play an important role leading to the formation of the **13a** (parallel, T-shaped) – Pb^{2+} picrate complex.

Figure 3 shows conformations of (a) **13a** (parallel) – Ag^{+} and (b) **13a** (anti-parallel) – Ag^{+} picrate complexes obtained by the same method as for **13a** – Pb^{2+} picrate complex.



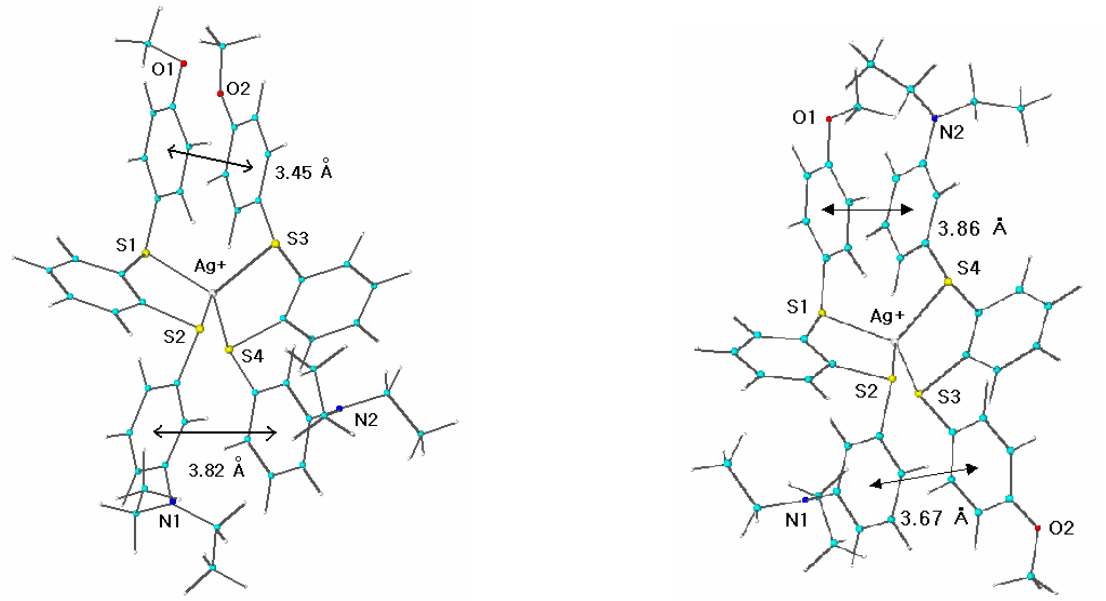
(a) (b)

Figure 3. Molecular mechanics-calculated conformations of (a) **13a** (parallel) – Ag^+ and (b) **13a** (anti-parallel) – Ag^+ picrate complexes.

The **13a** (parallel) – Ag^+ picrate complex shows that the Ag^+ ion forms a kind of tetrahedral geometry with four sulfur atoms. The non-bonded distances between two methoxyphenyl groups bonded to S1 and S3 atoms, and those of the two diisopropylaminophenyl groups bonded to S2 and S4 atoms of the **13a** (parallel) – Ag^+ picrate complex, obtained by the same method as for the **13a** – Pb^{2+} picrate complexes, are 3.31 and 4.14 Å, respectively. A π- π stacking interaction may be possible only between two methoxyphenyl groups. The HOMO – LUMO interaction energies between **13a** and Ag^+ ion and the thermodynamic energies of the **13a** (parallel) – Ag^+ and the **13a** (anti-parallel) – Ag^+ picrate complexes are summarized in Table 3. The data show that the latter has a smaller HOMO – LUMO interaction energy compared with that of the latter by 1.25 eV for α-spin and 1.31 eV for β–spin but it is less stable than the former by 14.33 kcal/mol. Accordingly, it may be difficult to predict a plausible conformation for the complex formed by **13a** and Ag^+ picrate based on the thermodynamic energy and the HOMO – LUMO interaction energy. Nevertheless, it may be envisaged that the lower thermodynamic energy as well as a smaller HOMO – LUMO interaction energy of the **13a** (parallel, T-shaped) – Pb^{2+} picrate complex compared with corresponding value for the **13a** – Ag^+ picrate complex may be responsible for a higher extractive ability of **13a** toward Pb^{2+} ion compared with Ag^+ ion.

Figure 4 shows conformation of (a) **7a** (parallel) – Ag^+ and (b) **7a** (anti-parallel) – Ag^+ picrate complexes obtained by the same method as for **13a** – Ag^+ picrate complex. The non-

bonded distances between two methoxyphenylgroups bonded to S1 and S3 atoms and two diethylaminophenyl groups bonded to S2 and S4 atoms



(a) (b)

Figure 4. Molecular mechanics-calculated conformations of (a) **7a** (parallel) – Ag^+ and (b) **7a** (anti-parallel) – Ag^+ picrate complexes.

of the **7a** (parallel) – Ag^+ picrate complex, determined by the same method as before, are 3.45 and 3.82 Å, respectively, which suggests possible π- π stacking interactions between two pairs of the phenyl rings. Similar calculations conducted on the **7a** (anti-parallel) – Ag^+ picrate complex show that the non-bonded distances between methoxyphenyl group bonded to S1 and diethylaminophenyl group bonded to S4, and diethylaminophenyl group bonded to S2 and methoxyphenyl group bonded to S3 atoms are 3.86 and 3.67 Å, respectively. The non-bonded distances between the phenyl groups of the **7a** (anti-parallel) – Ag^+ picrate complex are reasonable distances for π- π stacking interactions as is the case for the **7a** (parallel) – Ag^+ picrate complex. In the meantime, the calculated HOMO – LUMO interaction energies between **7a** and Ag^+ picrate and the thermodynamic energies of the **7a** – Ag^+ picrate complex are summarized in Table 4 (**7a** (parallel, T-stacking) – Ag^+ picrate complex is improbable).

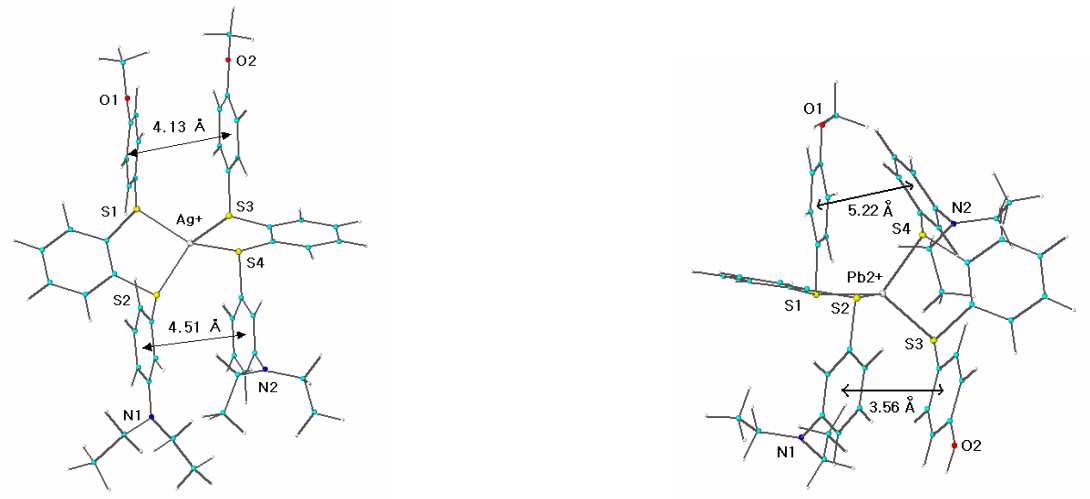
Table 4. The energy differences between the HOMO of **7a** and the LUMO of metal cations (Pb^{2+}, Ag^+) and the thermodynamic energies of **7a** – metal cation complexes at 25 °C

complex / energy	**7a** (P) – Ag^+	**7a** (A P) - Ag^+	**7a** (P) – Pb^{2+}	**7a** (A P) - Pb^{2+}

ΔE (HOMO – LUMO) eV	10.879 (α) 10.008 (β)	12.324 (α) 10.687 (β)	12.352 (α & β)	9.461 (α) 10.191 (β)
E (thermodynamic) kcal/mol	1,004.15	1,273.87	1,307.18	1,087.17

The data show that the **7a** (parallel) – Ag^+ picrate complex has a smaller HOMO – LUMO interaction energy than the **7a** (anti-parallel) – Ag^+ picrate complex by 1.4 eV for α -spin and 0.68 eV for β -spin. In addition, the former has a lower thermodynamic energy than the latter by 270 kcal/mol. Accordingly, it is conceivable that the formation of **7a** (parallel) – Ag^+ picrate complex is preferable to that of **7a** (anti-parallel) – Ag^+ picrate complex.

Figure 5 shows conformations of (a) **7a** (parallel) – Pb^{2+} and (b) **7a** (anti-parallel) – Pb^{2+} picrate complexes obtained by the same method as for **7a** – Ag^+ picrate complex. Non-bonded distances between two methoxyphenyl groups and two diethylaminophenyl groups of **7a** (parallel) – Pb^{2+} picrate complex are 4.13 and 4.51 Å, respectively, whereas those between two groups bonded to



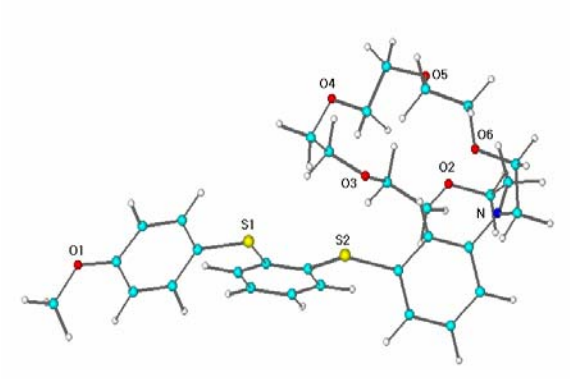
(a) (b)

Figure 5. Molecular mechanics-calculated conformations of (a) **7a** (parallel) – Pb^{2+} and (b) **7a** (anti-parallel) – Pb^{2+} picrate complexes.

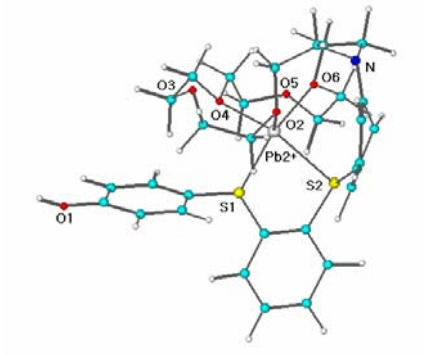
S1 and S4, and S2 and S3 of **7a** (anti-parallel) – Ag^+ picrate complex are 5.22 and 3.56 , respectively. The calculated HOMO –LUMO interaction energies between **7a** and Pb^{2+} picrate and the thermodynamic energies of the **7a** and Pb^{2+} picrate complexes are summarized in Table 4. The data show that the **7a** (anti-parallel) – Pb^{2+} picrate complex has smaller HOMO – LUMO interaction energies than the **7a** (parallel) – Ag^+ picrate complex by 2.9 eV for α-spin and 2.2 eV for β-spin. The former also has a lower thermodynamic energy than the latter by 220 kcal/mol. Consequently, it is conceivable that the formation of **7a** (anti-parallel) – Pb^{2+} picrate complex is preferable to that of **7a** (parallel) – Pb^{2+} picrate complex.

Although the HOMO – LUMO interaction energy of the **7a** (anti-parallel) – Pb^{2+} picrate complex is smaller than that of the **7a** (parallel) – Ag^{+} picrate complex, the latter shows a lower thermodynamic energy compared with that of the former, which may be reflected in the higher extractive ability of **7a** toward Ag^{+} ion compared with Pb^{2+} ion. The different tendencies of **7a** and **13a** with regard to complexing Ag^{+} and Pb^{2+} ions are envisaged to be due to the presence of the bulky diisopropylamino group as a substituent which makes two molecules of **13a** interact with Pb^{2+} ion to form a T-stacking complex so that the interaction energy between the HOMO of **13a** and the LUMO of Pb^{2+} ion becomes drastically smaller compared with those between the HOMO – LUMO of other host and guest pairs and the complex becomes remarkably stable.

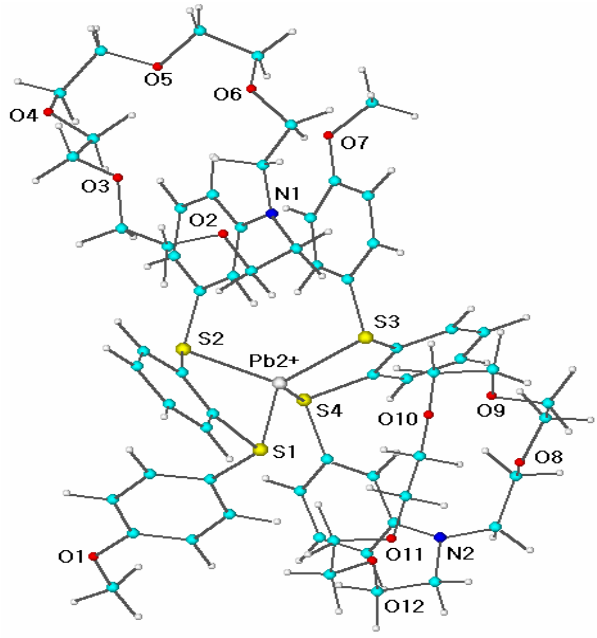
Compounds **7j** and **7m** having an aza-18-crown-6 moiety, respectively showed almost the same extractive abilities (67 and 66%, respectively) as that of **13a** toward Pb^{2+} ion. Surprisingly, aza-15-crown-5 and aza-18-crown-6, tethered sulfur-containing lariats at nitrogen atoms, have been seldom reported[16] despite the existence of numerous studies of other types of lariats. Examination of the molecular mechanics calculations on **7j** showed that a structure where the pendent arm is directed away from the azacrown has the lowest energy (E = 38.06 kcal/mol) (Figure 6, (a)). In this regard, the conformation is similar to the X-ray crystal structure of **14b** (Figure 1). The preparation of a single crystal for X-ray crystallography of **7j** - Pb^{2+} complex was unsuccessful. However, the molecular mechanics calculations indicate that the interactions of a Pb^{2+} ion with two sulfur and three oxygen atoms of one molecule of aza-18-crown-6 leads to a bent-type complex, which is the most stable complex having E = 29.76 kcal/mol (Figure 6, (b)). A sandwich-type complex in which two ligands accommodate a Pb^{2+} ion between two lariats of **7j** requires a higher energy by ca. 10 kcal/mol (E = 39.63 kcal/mol) (Figure 6, (c)). The increase in the extractive abilities of **7j** and **7m** toward Ag^{+} ion (40 and 24%, respectively) compared with that of **13a** (9%) may be ascribed to the oxygen atoms comprising aza-18-crown-6. Surprisingly, compound **18a** showed a very high selectivity toward Ag^{+} ion (86%), whereas its selectivity toward Pb^{2+} ion was comparable with those of **7e-f**. It is envisaged that two lariats, i.e., 3-[2-(4-methoxyphenylthio)-phenylthio]phenyl moieties, tethered



(a)



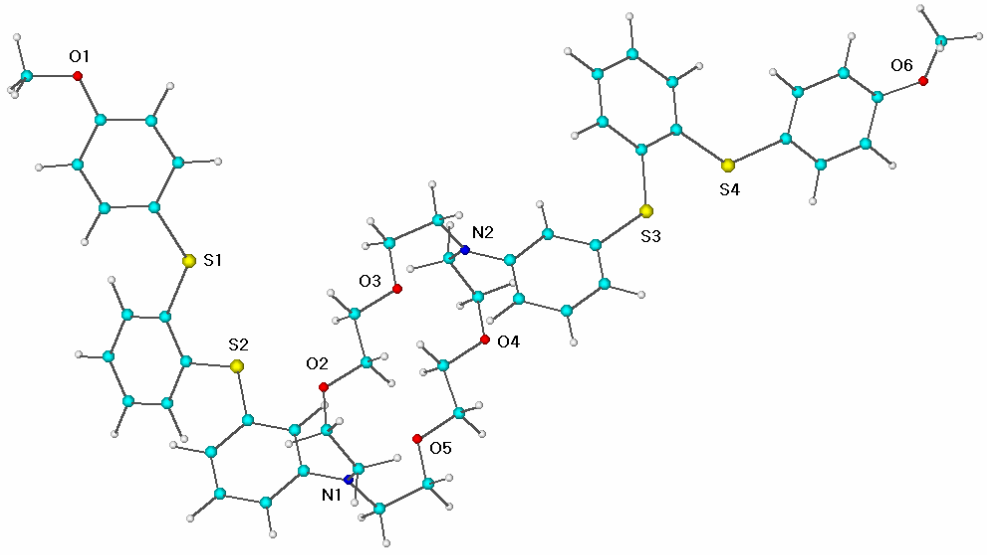
(b)



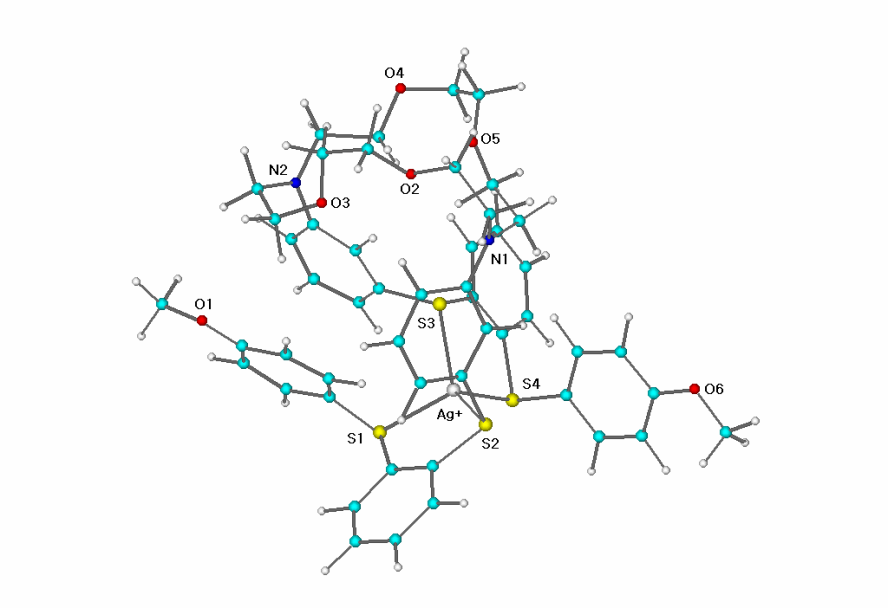
(c)

Figure 6. Molecular mechanics-calculated conformations of (a) the uncoordinated ligand **7j**, (b) the bent-type and (c) the sandwich-type **7j** - Pb^{2+} picrate complexes.

at the nitrogen of 7,16-diaza-18-crown-6, produce a strong interaction with an Ag^{+} ion (Figure 7, (b)), whereas the lariats were directed away from the cavity (Figure 7, (a)) as for **7a**, **7e-f**, or **7h** in the presence of Pb^{2+} ion which results in low extractive ability (12%).



(a)



(b)

Figure 7. Molecular mechanics-calculated conformations of (a) the uncoordinated ligand **18a** and (b) the **18a** - Ag^{+} picrate complex.

(b) Job plot of **7a**

Nine different concentrations of **7a** in $CHCl_3$ and the same number of differing concentrations of silver picrate were prepared. A Jobs plot was obtained by mixing five milliliters of two different solutions making up 2.4 x 10^{-4} M. Figure 6 shows that the highest absorbance was obtained when 1.6 x 10^{-4} M of **7a** was mixed with 8 x 10^{-5} M of aqueous silver picrate. Furthermore, the complex obtained from the chloroform layer showed a mass number (m/z) of 899.82 on the MALDI-TOF spectrum, corresponding to the molecular weight of a complex consisting of two molecules of **7a** and an Ag^{+} ion.

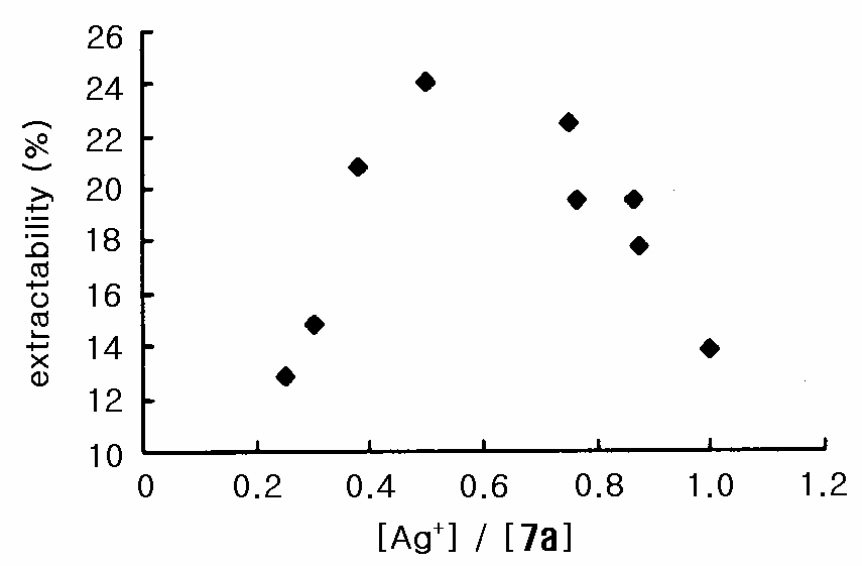


Figure 8. Extractability of **7a** for Ag^+ ion versus the mole fraction $[Ag^+]/[\mathbf{7a}]$.

(c) ^{1}H NMR study of the complexation of **7m** with Ag^+ and Pb^{2+} ions

The ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of **7m** was compared with those of the **7m** - Ag^+ and the **7m** - Pb^{2+} complexes. The comparison of the intensities of the aromatic protons of picrate appearing at 8.72 ppm with those of the methyl protons of the isopropyl group appearing at 1.35 ppm indicates the efficiency of the formation of the complex under the conditions in which the extractability experiment was performed. The ^{1}H NMR spectroscopic data showed 33 and 79% complexations toward Ag^+ and Pb^{2+} ions, respectively. These values are a little higher than 24 and 66%, respectively, which were obtained from the extractability experiments.

A noteworthy feature is that there is little difference in the shape of a multiplet appearing at 3.55 - 3.67 ppm, assigned to 24 methylene protons of **7m** and **7m** - Ag^+ complex, but significantly different shapes were observed in the multiplets of the aromatic proton signals. In contrast, the **7m** - Pb^{2+} complex exhibited a multiplet in the range of 3.32 - 3.85 ppm. The range observed from the latter complex is wider than that observed from the **7m** - Ag^+ complex. Furthermore, the shape differed considerably from that of the **7m** - Ag^+ complex but the shapes of the aromatic proton signals of the **7m** - Ag^+ and **7m** - Pb^{2+} complexes appeared similar. The results indicate that Ag^+ ion does not interact strongly with aza-18-crown-6 ring but Pb^{2+} interacts strongly with the same ring. This view is in good agreement with the similar extractabilities of **7a**, **7h**, and **7m** toward Ag^+ ion (Table 2) and the large difference in the extractabilities between **7a** or **7h** and **7m** toward Pb^{2+} ion.

In summary, 5-arylthianthrenium perchlorates **2** reacted with secondary alkylamines in the presence of LDA in THF at reflux temperature to give 2-(arylthio)-3'-(dialkylamino)diphenyl sulfides **7** as major products via a benzyne intermediate. In addition, 2-(arylthio)-2'-(dialkylamino)diphenyl sulfides **8** and thianthrene were formed depending on the structures of amines employed and the concentrations of LDA. The affinity of selected metal cations to

sulfides **7a**, **7e-f**, **7h**, **7j**, **7m**, **10**, **13a**, and **18a** was examined by an extraction method. Compounds **13a**, **7j**, **7m** showed 66 – 67% extractive abilities toward Pb^{2+} ions, and compound **18a** showed 86% extractive ability toward Ag^{+} ions.

Experimental Section

General Procedures. The ^{1}H and ^{13}C NMR spectra were recorded 300 MHz and 75 MHz, respectively in $CDCl_3$ or DMSO-d_6 solution containing Me_4Si as internal standard. IR spectra were recorded in KBr or film on KBr plates. Elemental analyses were determined by the Korea Basic Science Center. MALDI-TOF and FAB mass spectra were determined by National Center for Inter-University Research Facilities. Column chromatography was performed using silica gel (230-400 mesh, Merck). Melting points were measured on Fisher-Jones melting point apparatus and uncorrected. 5-Arylthianthrenium perchlorates (**2**) were prepared by the literature methods.[2] Amines were dried as reported in the literature.[17]

General procedure for the reactions of 2 with alkylamines

(a) To a solution of alkylamine in THF (20 mL) was added NaH (1.64 mmol) under nitrogen atmosphere. The solution was stirred for 20 min at room temperature, followed by the addition of **2**. The mixture was additionally stirred for an appropriate hour at reflux. Removal of the solvent in vacuo gave a residue, which was chromatographed on silica gel (7 x 1.5 cm). Elution with a mixture of EtOAc and hexane (1 : 9) gave thianthrene (**9**) and desired compounds **7** and **8**. Quantities of **2** and NaH, and yields of **7**, **8**, and **9** are summarized in Table 1.

(b) To a solution of alkylamine in THF (50 mL) was added **2**. The mixture was heated at reflux under nitrogen atmosphere, followed by the addition of 0.3 mL (0.6 mmol) of LDA (2 M, hexane) six to eight times at the intervals of 40 min using a hypodermic syringe. Removal of the solvent in vacuo gave a residue, which was chromatographed on silica gel (7 x 1.5 cm) as described in (a).

3'-(Diethylamino)-2-(4-methoxyphenylthio)diphenyl sulfide (7a). Oily liquid; ^{1}H NMR δ 1.17 (t, J = 7.1 Hz, 6H), 3.36 (q, J = 7.0 Hz, 4H), 3.86 (s, 3H), 6.57 (dd, J = 8.4, 2.5 Hz, 1H), 6.62 (d, J = 7.5 Hz, 1H), 6.63 (s, 1H), 6.86-6.92 (m, 3H), 7.00-7.03 (m, 2H), 7.14 (t, J = 8.1 Hz, 1H), 7.19-7.22 (m, 1H), 7.41 (d, J = 8.4 Hz, 2H); ^{13}C NMR δ 12.5, 44.3, 55.3, 110.8, 114.2, 115.1, 118.0, 123.6, 126.1, 127.3, 128.3, 130.0, 131.7, 134.7, 135.1, 135.8, 140.5, 148.4, 160.0; IR (neat) 3048, 2968, 1589, 1489, 1434, 1347, 1251, 1171 cm^{-1}; MS (EI) m/z 395 (M^{+}, 55), 380 (100), 256 (8), 216 (24), 190 (28). Anal. Calcd for $C_{23}H_{25}NOS_2$: C, 69.83; H, 6.37; N, 3.54; S, 16.21. Found: C, 69.69; H, 6.29; N, 3.49; S, 16.32.

2-(4-Methoxyphenylthio)-3'-(pentylamino)diphenyl sulfide (7b). Oily liquid; ^{1}H NMR δ 0.93 (m, 3H), 1.34-1.61 (m, 6H), 3.08 (t, J = 7.1 Hz, 2H), 3.85 (s, 3H), 6.52 (dd, J = 8.2, 1.6 Hz, 1H), 6.62 (t, J = 2.0 Hz, 1H), 6.68 (dd, J = 7.8, 1.7 Hz, 1H), 6.89-6.95 (m, 3H), 7.07 (m, 2H), 7.14 (t, J = 7.9 Hz, 1H), 7.24 (m, 1H), 7.45 (d, J = 6.7 Hz, 2H), A NH proton signal is invisible; ^{13}C

NMR δ 14.5, 22.9, 29.6, 29.7, 44.3, 55.7, 112.2, 115.3, 115.6, 120.1, 124.1, 126.6, 127.9, 128.9, 130.3, 132.5, 134.9, 135.8, 136.2, 141.2, 149.7, 160.4; IR (neat) 3400, 2912, 1582, 1482, 1434, 1280, 1250, 1160, 1027 cm^{-1}; MS (EI) *m*/*z* 409 (M^+, 50), 352 (5), 270 (14), 244 (12), 216 (100), 176 (34). Anal. Calcd for $C_{24}H_{27}NOS_2$: C, 70.21; H, 6.60; N, 3.68; S, 15.61. Found: C, 70.32; H, 6.70; N, 3.40; S, 15.67.

2-(4-Methoxyphenylthio)-3'-(*p*-toluidino)diphenyl sulfide (7c). Oily liquid; ^{1}H NMR δ 2.19 (s, 3H), 3.72 (s, 3H), 5.53 (s, 1H), 6.73-6.87 (m, 8H), 6.94-7.00 (m, 4H), 7.06 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.30 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR δ 29.7, 55.4, 115.0, 115.2, 117.7, 119.3, 121.8, 123.4, 126.1, 128.1, 128.2, 129.8, 129.9, 131.3, 133.0, 133.2, 136.1, 136.4, 139.6, 142.2, 144.9, 160.1; IR (neat) 3376, 3040, 2936, 1578, 1506, 1483, 1435, 1280, 1250, 1026 cm^{-1}; MS (EI) *m*/*z* 429 (M^+, 100), 214 (24), 106(90). Anal. Calcd for $C_{26}H_{23}NOS_2$: C, 72.69; H, 5.40; N, 3.26; S, 14.92. Found: C, 72.58; H, 5.43; N, 3.29; S, 14.85.

3'-[(2-Aminoethyl)amino]-2-(4-methoxyphenylthio)diphenyl sulfide (7d). Oily liquid; ^{1}H NMR δ 2.66 (br, s, 2H), 2.95 (t, *J* = 5.3 Hz, 2H), 3.19 (t, *J* = 5.4 Hz, 2H), 3.85 (s, 3H), 6.56 (d, *J* = 7.4 Hz, 1H), 6.65 (s, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 6.89-6.96 (m, 3H), 7.05-7.16 (m, 3H), 7.25 (m, 1H), 7.44 (dd, *J* = 6.7, 2.1 Hz, 2H), A NH proton signal is invisible; ^{13}C NMR δ 40.9, 45.4, 55.8, 112.4, 115.2, 115.6, 120.2, 123.8, 126.6, 128.1, 128.8, 130.5, 132.7, 134.3, 136.0, 136.3, 141.4, 149.3, 160.5; IR (neat) 3353, 3053, 2935, 1591, 1490, 1247, 1031 cm^{-1}; MS (EI) *m*/*z* 339 (M^+, 43), 215 (6), 200 (76). Anal. Calcd for $C_{21}H_{22}N_2OS_2$: C, 65.93; H, 5.80; N, 7.32; S, 16.76. Found: C, 65.89; H, 5.83; N, 7.25; S, 16.63.

2-(4-Methoxyphenylthio)-3'-(dipropylamino)diphenyl sulfide (7e). Oily liquid; ^{1}H NMR δ 0.85 (t, *J* = 7.4 Hz, 6H), 1.54 (sextet, *J* = 7.6 Hz, 4H), 3.15 (t, *J* = 7.6 Hz, 4H), 3.79 (s, 3H), 6.49-6.54 (overlap of s and dd, 2H), 6.60 (d, *J* = 7.7 Hz, 1H), 6.84-6.87 (m, 1H), 6.90 (d, *J* = 8.6 Hz, 2H), 7.01-7.05 (m, 2H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.24-7.27 (m, 1H), 7.41 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR δ 11.9, 20.8, 53.3, 55.8, 110.9, 113.9, 115.6, 117.8, 124.0, 126.5, 128.1, 128.5, 130.3, 133.0, 134.4, 135.9, 136.5, 141.9, 149.3, 160.5; IR (neat) 3040, 2944, 2872, 1579, 1483, 1434, 1355, 1282, 1246, 1029 cm^{-1}; MS (EI) *m*/*z* 423 (M^+, 32), 394 (100), 216 (37). Anal. Calcd for $C_{25}H_{29}NOS_2$: C, 70.88; H, 6.90; N, 3.31; S, 15.14. Found: C, 70.73; H, 6.82; N, 3.15; S, 15.29.

3'-(Dibutylamino)-2-(4-methoxyphenylthio)diphenyl sulfide (7f). Oily liquid; ^{1}H NMR δ 0.90 (t, *J* = 7.5 Hz, 6H), 1.28 (m, 4H), 1.49 (m, 4H), 3.19 (t, *J* = 7.7 Hz, 4H), 3.83 (m, 3H), 6.50-6.53 (overlap of s and dd, 2H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.86 (m, 1H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.05 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 7.27 (m, 1H), 7.42 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 14.4, 20.7, 29.8, 51.2, 55.8, 110.8, 113.8, 115.5, 117.7, 124.0, 126.4, 128.1, 128.5, 130.2, 132.9, 134.4, 135.9, 136.4, 141.8, 149.2, 160.5; MS (EI) *m*/*z* 451 (M^+, 37), 408 (100), 366 (41), 216 (51), 183 (29). Anal. Calcd for $C_{27}H_{33}NOS_2$: C, 71.80; H, 7.36; N, 3.10; S, 14.20. Found: C, 71.66; H, 7.27; N, 2.98; S, 14.26.

3'-(Morpholino)-2-(4-methoxyphenylthio)diphenyl sulfide (7g). Oily liquid; ^{1}H NMR δ 3.04 (t, *J* = 4.8 Hz, 4H), 3.72 (m, 7H), 6.71-6.74 (m, 2H), 6.81-6.84 (m, 4H), 6.95-6.99 (m, 2H), 7.10-7.16 (m, 2H), 7.33 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR δ 48.8, 55.1, 66.6, 114.2, 114.9, 117.6, 122.1, 123.3, 125.9, 127.6, 128.2, 129.6, 132.0, 133.7, 135.5, 135.7, 141.0, 151.7, 159.9; IR (neat)

3040, 2944, 2816, 1582, 1565, 1478, 1435, 1251, 1168, 1118 cm^{-1}; MS (EI) *m*/*z* 409 (M^+, 100), 351 (23), 270 (11), 242 (9), 216 (10), 200 (12), 184 (37). Anal. Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.45; H, 5.66; N, 3.42; S, 15.66. Found: C, 67.25; H, 5.58; N, 3.39; S, 15.57.

2-(4-Methoxyphenylthio)-3'-(piperidino)diphenyl sulfide (7h). Oily liquid; ^{1}H NMR δ 1.55 (m, 2H), 1.65 (m, 4H), 3.11 (t, *J* = 5.4 Hz, 4H), 3.78 (s, 3H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.82 (dd, *J* = 8.2, 2.1 Hz, 1H), 6.89 (m, 3H), 6.97 (s, 1H), 6.99-7.05 (m, 2H), 7.13-7.21 (m, 2H), 7.41-7.38 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR δ 24.7, 26.2, 50.7, 55.8, 115.6, 115.9, 119.5, 122.3, 124.1, 126.7, 127.9, 129.0, 130.2, 132.1, 135.3, 135.5, 136.2, 140.8, 153.2, 160.5; IR (neat) 3048, 2920, 2824, 1578, 1475, 1438, 1282, 1248, 1024 cm^{-1}; MS (EI) *m*/*z* 407 (M^+, 100), 268 (33), 216 (13), 184 (29). Anal. Calcd for $C_{24}H_{25}NOS_2$: C, 70.72; H, 6.18; N, 3.44; S, 15.73. Found: C, 70.59; H, 6.23; N, 3.27; S, 15.85.

13-[3-{2-(4-Methoxyphenylthio)phenylthio}phenyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (7i). Oily liquid; ^{1}H NMR δ 3.55 (m, 4H), 3.63 (m, 16H), 3.83 (s, 3H), 6.63 (m, 3H), 6.91 (m, 3H), 7.05 (m, 2H), 7.15-7.26 (m, 2H), 7.43 (d, *J* = 8.9 Hz, 2H); IR (neat) 2864, 1579, 1483, 1435, 1373, 1346, 1282, 1245, 1115, 1027 cm^{-1}. Anal. Calcd for $C_{29}H_{35}NO_5S_2$: C, 64.30; H, 6.51; N, 2.59; S, 11.84. Found: C, 64.37; H, 6.39; N, 2.46; S, 11.75.

16-[3-{2-(4-Methoxyphenylthio)phenylthio}phenyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (7j). Oily liquid; ^{1}H NMR δ 3.48-3.58 (m, 24H), 3.73 (s, 3H), 6.53 (m, 3H), 6.79 (m, 1H), 6.38 (dd, *J* = 6.7, 2.2 Hz, 2H), 6.94-6.98 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.13 (m, 1H), 7.33 (dd, *J* = 6.7, 2.2 Hz, 2H); IR (neat) 3040, 2848, 1579, 1482, 1435, 1344, 1280 cm^{-1}. Anal. Calcd for $C_{31}H_{39}NO_6S_2$: C, 64.68; H, 5.08; N, 2.43; S, 11.14. Found: C, 64.54; H, 4.99; N, 2.33; S, 11.26.

13-[3-{2-(2,4-Dimethoxyphenylthio)phenylthio}phenyl]-1,4,7,10-tetraoxa-13-azacyclopentadecane (7k). Oily liquid; ^{1}H NMR δ 3.23 (t, *J* = 4.67 Hz, 4H), 3.38 (t, *J* = 4.8 Hz, 4H), 3.47 (m, 4H), 3.55 (m, 4H), 3.62 (m, 4H), 3.71 (s, 3H), 3.77 (s, 3H), 6.45 (d, *J* = 8.8 Hz, 1H), 6.47 (s, 1H), 6.69 (d, *J* = 7.8 Hz, 1H), 6.92-7.01 (m, 5H), 7.16-7.25 (m, 3H); IR (neat) 2960, 1596, 1497, 1475, 1386, 1273, 1245, 1190, 1053, 1011, 784 cm^{-1}. Anal. Calcd for $C_{30}H_{37}NO_6S_2$: C, 63.02; H, 6.52; N, 2.45; S, 11.21. Found: C, 62.87; H, 4.64; N, 2.35; S, 11.37.

16-[3-{2-(2,4-Dimethoxyphenylthio)phenylthio}phenyl]-1,4,7,10,13-pentaoxa-16-azacyclooctadecane (7l). Oily liquid; ^{1}H NMR δ 3.51-3.59 (m, 24H), 3.72 (s, 3H), 3.76 (s, 3H), 6.43-6.58 (m, 5H), 6.72 (m, 1H), 6.97 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.14 (m, 1H), 7.25 (d, *J* = 8.2 Hz, 1H); IR (neat) 3296, 2912, 2208, 1616, 1568, 1488, 1459, 1276, 1248, 1212, 1177, 1136, 1043, 1017, 829, 809, 777 cm^{-1}. Anal. Calcd for $C_{32}H_{41}NO_7S_2$: C, 62.41; H, 6.71; N, 2.27; S, 10.41. Found: C, 62.53; H, 6.68; N, 2.33; S, 10.36.

16-[3-{2-(4-Isopropoxyphenylthio)phenylthio}phenyl]-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (7m). Oily liquid; ^{1}H NMR δ 1.35 (d, *J* = 6.1 Hz, 6H), 3.55-3.67 (m, 24H), 4.57 (hept, *J* = 6.1 Hz, 1H), 6.64 (m, 3H), 6.89 (m, 3H), 7.04 (m, 2H), 7.14 (t, *J* = 7.9 Hz, 1H), 7.21 (m, 1H), 7.40 (d, *J* = 8.8 Hz, 2H); IR (neat) 2864, 1579, 1478, 1437, 1374, 1346, 1275, 1242, 1110 cm^{-1}. Anal. Calcd for $C_{33}H_{43}NO_6S_2$: C, 64.57; H, 7.06; N, 2.28; S, 10.45. Found: C, 64.39; H, 6.87; N, 2.34; S, 10.69.

16-[3-{2-(4-*tert*-Butyl-3-methoxyphenylthio)phenylthio}phenyl]-1,4,7,10,13-pentaoxa-16-azacyclo-octadecane (7n). Oily liquid; ^{1}H NMR δ 1.12 (s, 9H), 3.54-3.68 (m, 24H), 3.88 (s,

3H), 6.65-6.73 (m, 3H), 6.97 (m, 2H), 7.05-7.19 (m, 6H); IR (neat) 2944, 2856, 1579, 1478, 1442, 1392, 1107 cm^{-1}. Anal. Calcd for $C_{35}H_{47}NO_6S_2$: C, 65.49; H, 7.38; N, 2.18; S, 9.99. Found: C, 65.71; H, 7.28; N, 2.31; S, 9.92.

2'-(Diethylamino)-2-(4-methoxyphenylthio)diphenyl sulfide (8a). Oily liquid; ^1H NMR δ 1.00 (t, *J* = 7.1 Hz, 6H), 3.05 (q, *J* = 7.1 Hz, 4H), 3.75 (s, 3H), 6.63 (d, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 7.8 Hz, 1H), 6.83-6.89 (m, 3H), 6.98-7.10 (m, 4H), 7.35 (m, 3H); ^{13}C NMR δ 12.5, 47.8, 55.4, 115.2, 123.0, 123.3, 124.5, 125.6, 125.9, 127.1 (overlap of two carbons), 128.9, 130.6, 135.9, 136.2, 136.8, 145.7, 148.2, 160.3; IR (neat) 3051, 2969, 2930, 2833, 1585, 1491, 1441, 1368, 1247, 1174, 1031 cm^{-1}; MS (EI) *m*/*z* 395 (M^+, 100), 380 (42), 366 (19), 256 (9), 240 (27), 227 (66), 216 (22), 164 (55). Anal. Calcd for $C_{23}H_{25}NOS_2$: C, 69.83; H, 6.37; N, 3.54; S, 16.21. Found: C, 69.76; H, 6.28; N, 3.39; S, 16.33.

2'-(Morpholino)-2-(4-methoylphenylthio)diphenyl sulfide (8g). Oily liquid; ^1H NMR δ 3.03 (t, *J* = 4.8 Hz, 4H), 3.76 (m, 7H), 6.68 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.84-6.89 (m, 3H), 6.98-7.10 (m, 4H), 7.29-7.36 (m, 3H); ^{13}C NMR δ 52.5, 55.8, 67.8, 115.6, 120.4, 123.3, 125.0, 126.2, 127.0, 127.8, 128.3, 129.4, 130.4, 133.2, 135.7, 137.1, 145.5, 150.3, 160.7; IR (neat) 3054, 2959, 2852, 1588, 1463, 1412, 1248, 1114, 1034 cm^{-1}; MS (EI) *m*/*z* 409 (M^+, 100), 350 (30), 270 (23), 242 (75), 212 (36), 180 (80). Anal. Calcd for $C_{23}H_{23}NO_2S_2$: C, 67.45; H, 5.66; N, 3.42; S, 15.66. Found: C, 67.58; H, 5.59; N, 3.31; S, 15.64.

2-(4-Methoxylphenylthio)-2'-(piperidino)diphenyl sulfide (8h). Oily liquid; ^1H NMR δ 1.56 (m, 2H), 1.71 (m, 4H), 3.01 (t, *J* = 5.1 Hz, 4H), 3.82 (s, 3H), 6.71 (dd, *J* = 7.9, 1.1 Hz, 1H), 6.81 (dd, *J* = 7.8, 1.3 Hz, 1H), 6.88-6.93 (m, 3H), 7.04-7.20 (m, 4H), 7.37-7.43 (m, 3H); ^{13}C NMR δ 24.8, 26.9, 53.8, 55.8, 115.6, 120.4, 123.6, 124.2, 126.1, 126.7, 127.7, 127.8, 129.2, 130.9, 133.5, 135.9, 137.1, 145.7, 151.7, 161.7; IR (neat) 3040, 2920, 2832, 1579, 1483, 1458, 1435, 1246, 1026 cm^{-1}; MS (EI) *m*/*z* 407 (M^+, 76), 350 (6), 268 (34), 242 (17), 216 (39), 190 (100). Anal. Calcd for $C_{24}H_{25}NOS_2$: C, 70.72; H, 6.18; N, 3.44; S, 15.73. Found: C, 70.58; H, 6.32; N, 3.37; S, 15.75.

***N*,*N*'-Bis[3-{2-(4-methoxyphenylthio)phenylthio}phenyl]ethylenediamine (12).** Oily liquid; ^1H NMR δ 3.11 (m, 4H), 3.85 (s, 6H), 6.78-6.96 (m, 10H), 7.04-7.08 (m, 4H), 7.28-7.41 (m, 4H), 7.41-7.57 (m, 6H), Two NH proton signals are invisible; ^{13}C NMR δ 41.0, 44.8, 54.9, 112.4, 115.3, 115.6, 120.1, 124.0, 125.9, 128.1, 129.1, 130.5, 132.7, 134.3, 136.1, 136.3, 141.4, 149.3, 160.4; IR (neat) 3054, 2968, 2929, 2873, 2352, 1587, 1492, 1442, 1288, 1247, 1172, 1033 cm^{-1}. Anal. Calcd for $C_{40}H_{36}N_2O_2S_4$: C, 68.15; H, 5.15; N, 3.97; S, 18.19.

3'-(Diisopropylamino)-2-(4-methoxyphenylthio)diphenyl sulfide (13a). mp 152-154 δ (*n*-hexane-CH_2Cl_2); ^1H NMR δ 3.29 (s, 8H), 3.82 (s, 6H), 6.81-6.94 (m, 10H), 6.97 (s, 2H), 7.01-7.10 (m, 4H), 7.20-7.26 (m, 4H), 7.41 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 49.3, 55.8, 115.4, 115.6, 118.8, 122.7, 123.9, 126.6, 128.2, 130.3, 132.7, 134.3, 136.1, 136.3, 141.6, 152.1, 160.5; IR (neat) 3088, 3024, 1750, 1654, 1600, 1443, 1360, 1283, 1254, 1084, 877, 752 cm^{-1}; FAB MS (EI) *m*/*z* 730 (M^+). Anal. Calcd for $C_{42}H_{38}N_2O_2S_4$: C, 69.01; H, 5.24; N, 3.83; S, 17.55. Found: C, 68.74; H, 5.45; N, 3.68; S, 17.81.

3'-(Dipropylamino)-2-[(4-dipropylamino)phenylthio]diphenyl sulfide (14a). Oily liquid; ^{1}H NMR δ 0.85 (t, *J* = 7.5 Hz, 6H), 0.94 (t, *J* = 7.3 Hz, 6H), 1.59 (m, 8H), 3.15 (t, *J* = 7.8 Hz, 4H), 3.25 (t, *J* = 7.6 Hz, 4H), 6.48-6.53 (overlap of s and dd, 2H), 6.59-6.64 (overlap of d and d, 3H), 6.81 (dd, *J* = 7.8, 1.5 Hz, 1H), 6.97 (td, *J* = 7.5, 1.5 Hz, 1H), 7.05 (td, *J* = 7.5, 1.6 Hz, 1H), 7.12 (t, *J* = 7.8 Hz, 1H), 7.25 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.34 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR δ 11.39, 11.42, 20.4 (overlap), 52.8, 52.9, 110.2, 112.4, 113.1, 114.9, 116.9, 125.0, 126.5, 127.8, 129.7, 131.7, 132.9, 135.9, 137.0, 144.1, 148.7, 148.8; IR (neat) 3048, 2944, 2856, 1582, 1493, 1357, 1094, 1030 cm^{-1}; MS (EI) *m*/*z* 492 (M^+, 98), 463 (83), 232 (18), 217 (100), 184 (40). Anal. Calcd for $C_{30}H_{40}N_2S_2$: C, 73.12; H, 8.18; N, 5.68; S, 13.01. Found: C, 73.01; H, 8.29; N, 5.49; S, 13.23.

3'-(Morpholino)-2-(4-morpholinophenylthio)diphenyl sulfide (14b). mp 120-121 °C (*n*-hexane-CH_2Cl_2); ^{1}H NMR δ 3.03 (m, 4H), 3.10 (m, 4H), 3.74 (m, 8H), 6.69-6.73 (m, 2H), 6.76-6.84 (m, 4H), 6.90-7.00 (m, 2H), 7.09-7.16 (m, 2H), 7.30 (d, *J* = 6.9 Hz, 2H); ^{13}C NMR δ 49.0, 49.4, 67.1, 67.2, 114.8, 116.5, 118.2, 121.9, 122.6, 126.4, 128.2, 128.4, 130.3, 132.8, 133.7, 136.3, 142.2, 151.8, 152.3; IR (neat) 3052, 2961, 2852, 1589, 1494, 1446, 1235, 1121 cm^{-1}; MS (EI) *m*/*z* 464 (M^+, 100), 232 (15), 216 (20), 184 (44). Anal. Calcd for $C_{26}H_{28}N_2O_2S_2$: C, 67.21; H, 6.07; N, 6.01; S, 13.80. Found: C, 67.46; H, 6.15; N, 6.01; S, 14.00.

3'-(Piperidino)-2-(4-piperidinophenylthio)diphenyl sulfide (14c). Oily liquid; ^{1}H NMR δ 1.55-1.72 (m, 12H), 3.12 (t, *J* = 5.4 Hz, 4H), 3.21 (t, *J* = 5.3 Hz, 4H), 6.76 (d, *J* = 7.5 Hz, 1H), 6.83 (m, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.96-7.02 (m, 3H), 7.14-7.18 (m, 2H), 7.36 (d, *J* = 8.9 Hz, 2H); ^{13}C NMR δ 24.7, 26.10, 26.14, 50.1, 50.7, 115.7, 117.0, 119.2, 120.3, 122.0, 126.1, 127.9, 128.1, 130.1, 132.3, 133.9, 135.7, 136.4, 142.3, 152.6, 153.2; IR (neat) 3040, 2912, 2840, 2792, 1586, 1491, 1438, 1374, 1230, 1123, 1019 cm^{-1}; MS (EI) *m*/*z* 460 (M^+, 100), 266 (12), 229 (28), 216 (20), 184 (30). Anal. Calcd for $C_{28}H_{32}N_2S_2$: C, 73.00; H, 7.00; N, 6.08; S, 13.92. Found: C, 73.23; H, 7.12; N, 5.93; S, 13.99.

2'-(Morpholino)-2-(4-morpholinophenylthio)diphenyl sulfide (15b). Oily liquid; ^{1}H NMR δ 3.03 (t, *J* = 4.5 Hz, 4H), 3.13 (t, *J* = 4.78 Hz, 4H), 3.78 (m, 8H), 6.68 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.75 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.89 (t, *J* = 7.9 Hz, 1H), 6.97-7.12 (m, 4H), 7.27-7.32 (m, 3H); ^{13}C NMR δ 48.9, 52.4, 67.2, 67.8, 116.5, 120.4, 121.5, 125.0, 126.0, 127.0, 127.6, 128.3, 129.3, 130.1, 133.3, 135.7, 136.8, 145.9, 150.3, 152.0; IR (neat) 3054, 2959, 2852, 1589, 1497, 1443, 1234, 1117 cm^{-1}; MS (EI) *m*/*z* 464 (M^+, 100), 242 (70), 216 (32), 180 (67). Anal. Calcd for $C_{26}H_{28}N_2O_2S_2$: C, 67.21; H, 6.07; N, 6.01; S, 13.80. Found: C, 67.17; H, 6.21; N, 5.87; S, 13.64.

***N,N'*-Bis[3-{2-(4-methoxyphenylthio)phenylthio}phenyl]piperazine (17).** Oily liquid; ^{1}H NMR δ 3.29 (s, 6H), 3.82 (s, 6H), 6.81-6.94 (m, 12H), 6.97 (m, 2H), 7.01-7.10 (m, 4H), 7.20-7.26 (m, 4H), 7.41 (d, J = 8.65 Hz, 4H); ^{13}C NMR δ 49.29, 55.76, 115.42, 115.56, 118.82, 122.70, 123.9, 126.5, 128.1, 128.8, 130.3, 132.7, 134.3, 136.1, 136.3, 141.6, 152.1, 160.5; IR (neat) 3408, 2928, 1693, 1565, 1472, 1443, 1405, 1325, 1283, 1232, 1184, 1094, 1030, 880 cm^{-1}. Anal. Calcd for $C_{42}H_{38}N_2O_2S_4$: C, 69.00; H, 5.24; N, 3.83; S, 17.54. Found: C, 69.12; H, 5.21; N, 3.66; S, 17.71.

7,16-Bis[3-{2-(4-methoxyphenylthio)phenylthio}phenyl]-1,4,10,13-tetraoxa-7,16-diazacyclo-octade-cane (18a). mp 141-144 °C (EtOH); ^{1}H NMR δ 3.50-3.64 (m, 24H), 3.82 (s, 6H), 6.56 (d, *J* = 8.5 Hz, 2H), 6.63 (overlap of s and d, 4H), 6.85-6.88 (m, 3H), 6.91 (d, *J* = 8.7 Hz, 2H), 6.99-7.08 (m, 4H), 7.14 (t, *J* = 7.9 Hz, 3H), 7.20-7.23 (m, 2H), 7.42 (d, *J* = 8.9 Hz, 4H); ^{13}C NMR δ 51.2, 55.4, 69.0, 70.9, 110.5, 113.7, 115.2, 118.4, 123.5, 126.1, 127.6, 128.2, 130.0, 132.2, 134.2, 135.6, 135.9, 141.1, 148.6, 160.1; IR (neat) 2856, 1579, 1480, 1434, 1246, 1099, 1026 cm^{-1}; FAB MS (EI) *m*/*z* 907 (M^+, 11). Anal. Calcd for $C_{50}H_{54}N_2O_6S_4$: C, 66.19; H, 6.00; N, 3.09; S, 14.14. Found: C, 66.09; H, 5.97; N, 2.99; S, 14.21.

7,16-Bis[3-{2-(2,4-dimethoxyphenylthio)phenylthio}phenyl]-1,4,10,13-tetraoxa-7,16-diazacyclo-octadecane (18b). mp 64-66 °C (EtOH); ^{1}H NMR δ 3.69-3.76 (m, 24H), 3.92 (s, 6H), 3.96 (s, 6H), 6.61-6.69 (m, 6H), 6.75 (m, 4H), 6.91 (m, 2H), 7.15 (m, 4H), 7.25 (t, *J* = 8.2, 2H), 7.35 (m, 2H), 7.45 (d, *J* = 8.3 Hz, 2H); IR (neat) 3408, 1568, 1437, 1091, 1030, 876, 790, 739 cm^{-1}; FAB MS (EI) *m*/*z* 967 (M^+, 12). Anal. Calcd for $C_{52}H_{58}N_2O_8S_4$: C, 64.57; H, 6.04; N, 2.90; S, 13.26. Found: C, 64.48; H, 6.17; N, 3.01; S, 13.39.

m-CPBA - mediated the oxidation of deuterated **10:** To a solution of deuterated **10** (103 mg, 0.32 mmol) in $CHCl_3$ (30 mL) was added excess *m*-CPBA. The mixture was stirred for 1 h at room temperature, followed by addition of K_2CO_3 (100 mg, 0.72 mmol), which was stirred for an additional 1 h. Saturated aqueous $NaHCO_3$ (50 mL) was added. The mixture was extracted with CH_2Cl_2 (30 mL x 3). The combined extract was dried over $MgSO_4$. Removal of the solvent in vacuo gave a residue, which was chromatographed on a silica gel (7 x 1.5 cm) using a mixture of EtOAc and hexane (1 : 9) to give a mixture of *m*-chlorobenzoic acid and unreacted *m*-CPBA. Subsequent elution with the same solvent mixture (1 : 3) gave 2-(4-methoxyphenylsulfinyl)diphenyl sulfone (**11**) (102 mg, 83%) : mp 121-125 °C (EtOH); ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.85 (s, 3H, CH_3O), 6.97 (d, *J* = 9.0 Hz, 2 x H2), 7.50 (m, 2H, H13 and H15), 7.57 (t, *J* = 6.87, 1H, H14), 7.80 (m, 2H, H7 and H8), 7.95 (m, 3H, H3, H12 or H16), 8.43 (m, 1H, H6 or H9), 8.49 (m, 1H, H6 or H9); ^{13}C NMR (75 MHz, $CDCl_3$) δ 55.6, 114.0, 127.9, 128.6, 128.8, 130.8, 132.8, 133.0, 133.1, 133.2, 133.6, 134.0, 139.8, 141.3, 141.6, 163.5 ; IR (KBr) 3392, 3008, 2928, 1594, 1507, 1491, 1379, 1309, 1270, 1245, 1178, 1052, 1018, 909, 880 cm^{-1}; MS (EI) *m*/*z* 389 (M^+, 40), 388 (9), 325 (18), 123 (100). Anal. Calcd for $C_{19}H_{15}DO_5S_2$; C, 58.60; H, 4.40; S, 16.46; Found: C, 57.84; H, 4.31; S, 16.33.

Determination of the extractive ability

The extraction of metal ions from the aqueous solution into $CHCl_3$ layer was performed in capped test tubes. For blank test, biphasic mixture (the volume of water and chloroform was 2 mL each) was vigorously stirred for 1 min and then kept at 25 ± 1 °C for 12 h. The concentration of picrate in the aqueous phase was determined by absorption spectroscopy at 354 nm. Likewise the concentration of picrate anion remained in the aqueous phase was determined by the same method. The extractive ability was calculated according to equation 1. All experiments were carried out in duplicate or triplicate and the respective results were averaged. The results are summarized in Table 2.

Crystal data for **14b**: $C_{26}H_{28}N_2O_2S_2$, M = 464.62, triclinic, a = 10.043(2), b = 11.070(2), c = 12.627(2) Å, α = 105.79(2), β = 110.56(2), γ = 102.20(2) °, U = 1189.2(4) Å^3, T = 293(2) K, P-1, Z = 2, μ (M_o - K $_\alpha$) = 0.250 mm^{-1}, λ = 0.71073 Å, 4180 reflections measured, 4179 unique (R_{int} = 0.0033) which were used in all calculations. Final R indices [$I > 2\ \delta\ (I)$]: $R1$ = 0.0615, $\omega R2$ = 0.1498. (CCDC 213883, See http://www.ccdc.cam.ac.uk/prods/encifer for crystallographic data in CIF or other format.)

Molecular mechanics calculations (MC/SD conformational searching with MacroModel version 5.0 utilizing MN2$^+$ force field). Selected bond distances and angles are in the supplemental section. The HOMO – LUMO interaction energies were calculated by HyperChem version 6.03 utilizing CNDO and ZINDO/1.[15]

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