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# Synthesis, Structure, and Complexation Behavior of 14- and 28-Membered Partially Unsaturated Thiacrown Ethers

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ABSTRACT: *Partially unsaturated 14- and 28-membered thiacrown ethers,* **3** *and* **4**, *which possess alternating Z-carbon–carbon double bonds and propylene chains, were synthesized by stepwise reactions. The crystal structure of larger cyclic compound* **4** *was determined by X-ray crystallographic analysis. 14-Membered thiacrown ether* **3** *was found to be more easily oxidized electrochemically than larger cyclic compound* **4** *and the corresponding saturated system. Compounds* **3** *and* **4** *isomerized at temperatures exceeding 100°C in solution to give cyclic compounds with E-olefin moieties but were stable at 80°C in solution. Compound* **3** *formed 1:1 complexes with silver and copper ions, and* **4** *formed 1:2 complexes mainly in solution. A complex of* **3** *with mercury(II) chloride was isolated, and its crystal structure was determined by X- ray analysis.* © 2011 Wiley Periodicals, Inc. Heteroatom Chem 22:287–293, 2011; View this article online at wileyonlinelibrary.com. DOI 10.1002/hc.20678

## INTRODUCTION

Following the synthesis of the first thiacrown ether by Meadow and Reid [1], thiacrown ethers of various sizes have been synthesized [2–4]. Unsaturated thiacrown ethers, of which all sulfur atoms are connected by carbon–carbon double bonds, were also isolated and their complexation behavior was studied [5–8]. Thiacrown ethers that possess both saturated and unsaturated bonds in their ring systems are also interesting compounds on comparison of their conformation, electrochemical properties, and complexation behaviors with those of the corresponding saturated or unsaturated compounds. Among the thiacrown ethers that possess both saturated and unsaturated bonds, some 14-membered cyclic compounds that possess alternating *Z*-carbon–carbon double bonds and propylene chains are known [9–15]. However, larger cyclic compounds featuring this system have not been synthesized so far. Recently, we succeeded in synthesizing a 28-membered partially unsaturated thiacrown ether along with a smaller one. We report herein the synthesis and crystal structures of the partially unsaturated thiacrown ethers, as well as their thermal and complexation behaviors.

## RESULTS AND DISCUSSION

### Synthesis of Partially Unsaturated Thiacrown Ethers

First of all, direct synthesis was attempted. When disodium *cis*-ethenedithiolate and 1,3-dibromopropane were stirred in acetonitrile solution, a seven-membered cyclic product, (*Z*)-3,7-dithiacycloheptene [16,17], was obtained together with a trace amount of the 1:2 adduct but the desired larger thiacrown ether was not obtained. Therefore, a stepwise synthesis was examined. The reaction of *cis*-ethenedithiolate with 2 equiv of 3-bromo-1-propanol in acetonitrile gave diol **1** (Scheme 1).

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Dedicated to Professor Kin-ya Akiba on the occasion of his 75th birthday.

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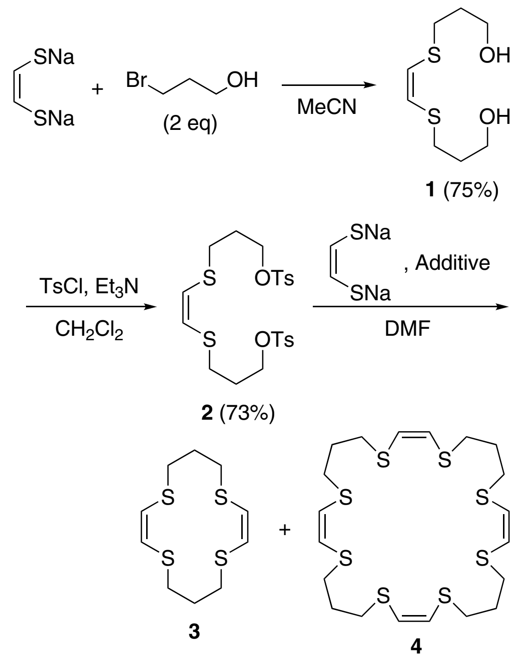


| Additive | Yield (%) | |
|---|---|---|
| | **3** | **4** |
| — | 3.8 | 12.4 |
| Na$_2$CO$_3$ | 5.8 | 16.0 |
| K$_2$CO$_3$ | 4.5 | 7.8 |
| Cs$_2$CO$_3$ | 7.0 | 14.0 |
| AgBF$_4$ | 2.5 | 8.2 |
| AgOTf | 1.5 | 6.6 |

**SCHEME 1** Synthesis of partially unsaturated thiacrown ethers.

After transformation of the hydroxyl group into tosylate, the reaction of **2** with *cis*-ethenedithiolate in dimethylformamide (DMF) solution afforded desired partially unsaturated 28-membered thiacrown ether **4**, together with a small amount of 14-membered thiacrown ether **3**. Compound **3** was previously synthesized by the reduction of the corresponding cyclodiyne by Gleiter and co-workers [11]. In acetonitrile solution, however, the reaction did not proceed. Expecting the template effect, the reactions were examined in the presence of several salts, such as sodium carbonate, potassium carbonate, cesium carbonate, silver tetrafluoroborate, and silver triflate. However, no remarkable improvement of the yield was observed. In these reactions, no 21-membered cyclic product was detected.

## *Crystal Structure of Partially Unsaturated Thiacrown Ether*

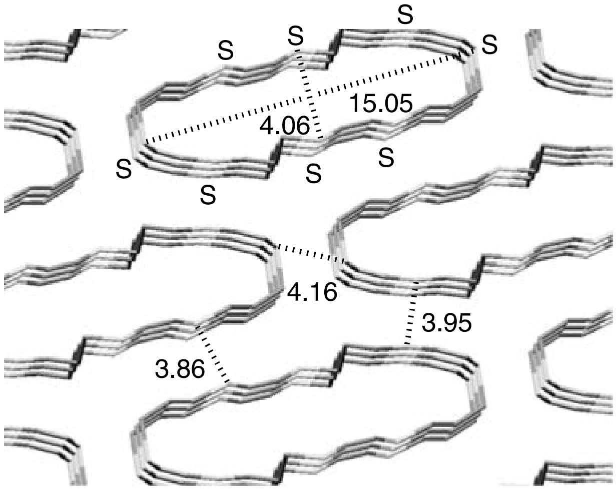


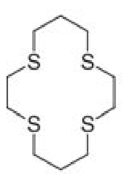
**FIGURE 1** Crystal structure of **4**. Hydrogen atoms are omitted for clarity. C($sp^2$)—S: 1.75–1.76 Å; C($sp^3$)–S: 1.81–1.82 Å; C—S—C: 99.5–100.3°; S—C=C—S: 0.6–1.0°.

The crystal structure of 28-membered partially unsaturated thiacrown ether **4** was determined by X-ray crystallographic analysis (Fig. 1). The X-ray analysis showed that all of the olefin moieties have the *Z*-geometry, and the bond lengths, bond angles, and dihedral angles are almost normal. It was also found that the molecule has a slender structure, and the atomic distance between the farthest sulfur atoms is 15.05 Å, which is nearly twice that of a 14-membered compound **3** [11]. The packing structure also showed a columnar structure. The distance between the stacked molecules is 5.23 Å, and the atomic distances between sulfur atoms of neighboring molecules are 3.86–4.16 Å, which are slightly longer than twice the van der Waals radii of sulfur.

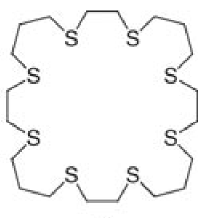
## *Electrochemistry of Partially Unsaturated Thiacrown Ethers*

Partially unsaturated thiacrown ethers **3** and **4** showed irreversible cyclic voltammograms (Fig. 2). The potential was scanned at 100 mVs$^{-1}$ versus Fc/Fc$^+$ toward negative and back again. Two oxidation peaks were observed for each macrocycle; compound **3** showed oxidation peaks at 0.35 and 0.79 V, and larger cyclic system **4** showed peaks at 0.52 and 0.87 V. These results indicate that smaller partially unsaturated thiacrown ether **3** is more easily oxidized than the larger one perhaps because the delocalization of the resulting cation effectively takes place in the 14-membered cyclic system by intramolecular interaction between the sulfur atoms. The oxidation potentials of saturated thiacrown ether **5** [18,19] were observed at 0.77 and 1.08 V under the same conditions, and it was found that the

14-membered partially unsaturated thiacrown ether **3** was more easily oxidized than the corresponding saturated **5**. A similar trend was also observed in the case of **4**; 28-membered saturated thiacrown ether **6** [20] showed two oxidation peaks at 0.73 and 1.02 V.



**5**



**6**

### *Thermal Stability and Isomerization of Partially Unsaturated Thiacrown Ethers*

When the thermal stability of **3** was examined in a nuclear magnetic resonance (NMR) tube, *Z*-*E*-isomerization of the olefin moieties was observed upon heating. Compound **3** was stable at 80°C but gradually decomposed at temperatures exceeding 100°C in dimethyl sulfoxide (DMSO)-$d_6$ to show new signals on the $^1$H NMR spectra assignable to *Z*-*E*-isomerized products **7** and **8** and ring-reduced seven-membered cyclic compound **9**. The changes in the $^1$H NMR spectra of the olefin protons of **3** are shown in Fig. 3. At 140°C, the isomerization reaction was accelerated and *E*, *Z*-isomer **7** was obtained up to 60% yield. Trace amounts of the isomers were isolated by silica-gel chromatography, and the structures were assigned on the basis of $^1$H and $^{13}$C NMR spectra. The structure of **7** was finally determined by X-ray analysis (Fig. 4). Larger partially unsaturated thiacrown ether **4** also reacted at temperatures exceeding 100°C, and the formation of *Z*-*E*-isomerized products was confirmed by $^1$H NMR measurements. However, the reaction was complicated, probably due to the existence of many double bonds in the molecule, and only a trace amount of *E*,*Z*,*Z*,*Z*-isomer **10** was obtained.

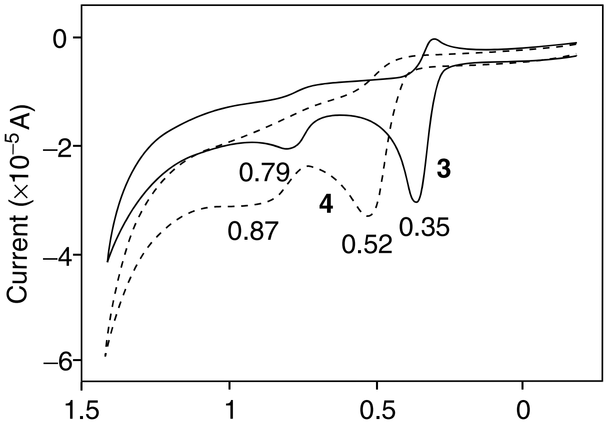
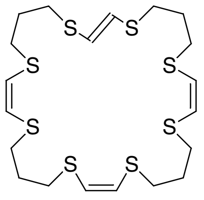


FIGURE 2 Cyclic voltammograms of **3** and **4** in acetonitrile.



**10**

To examine the molecular strains of the *Z*, *Z*-, *E*, *Z*-, and *E*, *E*-isomers of 14-membered partially unsaturated thiacrown ethers **3**, **7**, and **8**, a theoretical study was carried out. As a model molecule for comparison, 1,2-bis(ethylthio)ethene was calculated. The results showed that the *E*-isomer of the model molecule was more stable than the *Z*-isomer by 1.9 kcal mol$^{-1}$. In the case of the 14-membered cyclic compounds, *E*, *E*-isomer **8** was found to be more stable than *Z*, *Z*-isomer **3** by 3.8 kcal mol$^{-1}$, and *E*, *Z*-isomer **7** was also more stable than **3** by 1.6 kcal mol$^{-1}$. These values correspond well to the results of calculation for the model molecules, indicating that all of the isomers of the 14-membered cyclic compound have strain-free geometries. The crystal structures of **3** [11] and **7** also support this result.

### *Complexation Behavior of Partially Unsaturated Thiacrown Ethers*

In the cases of corresponding saturated 14- and 28-membered thiacrown ethers, silver complexes have been obtained [21–23]. We also examined the complexation of **3** and **4** with silver ion using silver trifluoroacetate and tetrafluoroborate in several solvents. However, no complex of **3** and **4** was obtained as the sole product. In solution, however, changes in the chemical shifts were observed on their $^1$H NMR spectra. Therefore, titration experiments for the complexation of **3** and **4** with silver ion were carried out in solution. The $^1$H signals of **3** and **4** shifted to lower field with the addition of silver trifluoroacetate in acetone–$d_6$. Job's plots of the complexation of **3** and **4** with silver trifluoroacetate are shown in Fig. 5; the chemical shifts of protons for sp$^3$-carbons neighboring sulfur atoms were used for the plots. The

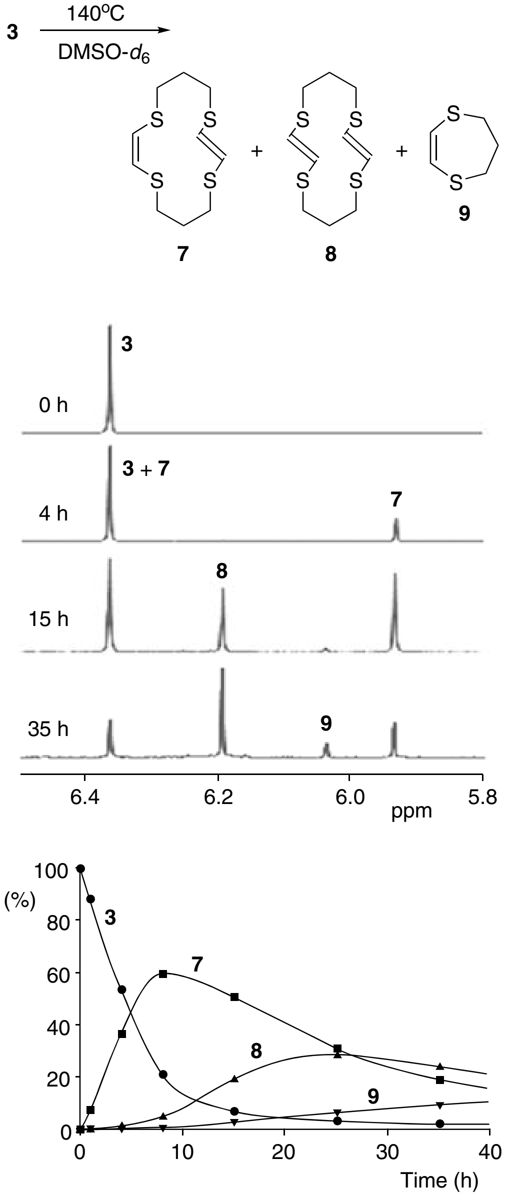


**FIGURE 3** Thermal *Z*-*E*-isomerization of partially unsaturated thiacrown ether **3** at 140°C.

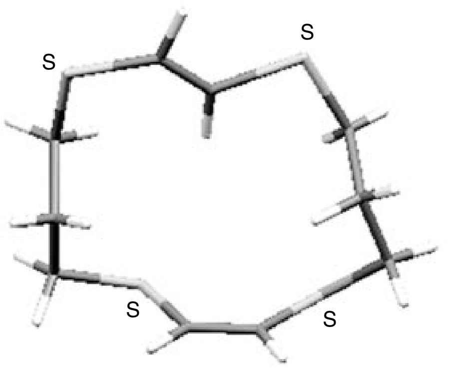


**FIGURE 4** Crystal structure of **7**. C($sp^2$)—S: 1.72–1.83 Å; C($sp^3$)—S: 1.78–1.82 Å; C—S—C: 98.8–106.3°; S—C=C—S(*E*-olefin): 171.9°; S—C=C—S(*Z*-olefin): −1.9°.

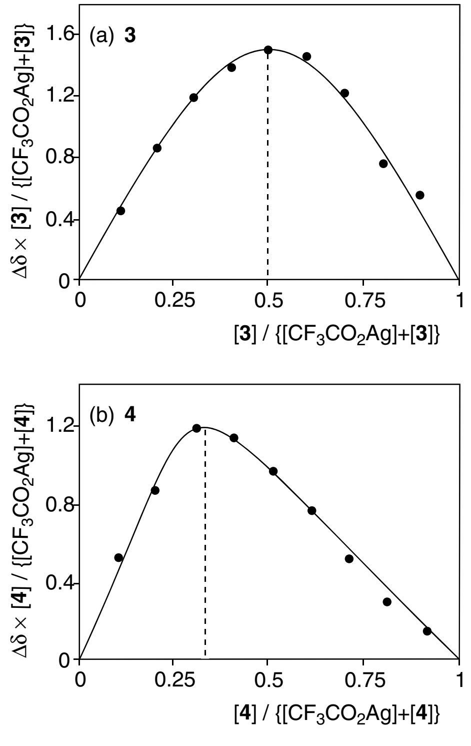


**FIGURE 5** Job's plots of (a) **3** and (b) **4** with silver trifluoroacetate in acetone-$d_6$.

results indicate that 14-membered thiacrown ether **3** forms a 1:1 complex with silver trifluoroacetate, and larger thiacrown ether **4** affords a 1:2 complex in acetone solution; these results are similar to those of the corresponding saturated systems obtained from the titration plots. Similar results were obtained in acetonitrile-$d_3$ solution. It was also found that compound **3** formed a 1:1 complex with copper(II) trifluoromethanesulfonate, and **4** gave a 1:2 complex mainly in acetone-$d_6$ solution.

In the complexation with mercury(II) chloride, 14-membered partially unsaturated thiacrown ether **3** afforded stable 1:2 complex **11**. The crystal structure was determined by X-ray analysis. The crystal structure demonstrated that two sulfur atoms coordinate to a mercury atom, as shown in Fig. 6; this structure is similar to that for the mercury complex of corresponding saturated 14-membered thiacrown ether **5** [24].

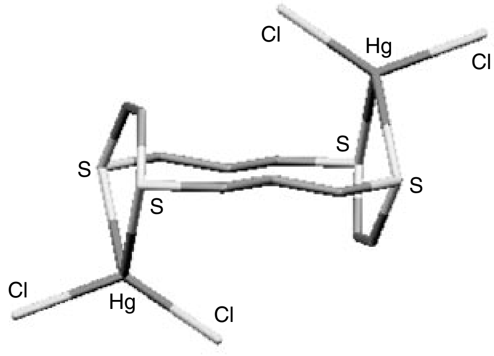


**FIGURE 6** Crystal structure of **11**. Hydrogen atoms are omitted for clarity. S—Hg: 2.66–2.72 Å; C(*sp*$^2$)—S: 1.76 Å; C(*sp*$^3$)—S: 1.72–1.83 Å; S—Hg—S: 78.8°; Cl—Hg—Cl: 125.0°; C—S—C: 99.4–99.6°.

## *CONCLUSION*

In this study, 14- and 28-membered partially unsaturated thiacrown ethers possessing alternating *Z*-carbon–carbon double bonds and propylene chains were synthesized. The 28-membered thiacrown ether was found to have a slender structure in the crystalline state. The 14-membered thiacrown ether was found to be more easily oxidized electrochemically than the 28-membered cyclic compound and the corresponding saturated system. The partially unsaturated thiacrown ethers isomerized at temperatures exceeding 100°C to give the *Z-E*-isomerized compounds but were stable at temperatures below 80°C in solution. The 14-membered thiacrown ether was also found to form 1:1 complexes with silver and copper ions, and the larger thiacrown ether formed 1:2 complexes mainly in solution.

## *EXPERIMENTAL*

### *Materials and Methods*

The saturated thiacrown ethers, 3,7,10,14-tetrathiacyclotetradecane (**5**) [18,19] and 3,7,10,14,17,21,24,28-octathiacyclooctacosane (**6**) [20] were synthesized according to the literature. All reactions were carried out under nitrogen. $^1$H, and $^{13}$C NMR spectra were recorded on JEOL JNM-EX-500, JEOL JNM-EX-400, or JEOL Excalibur-270 FT NMR system (JEOL Ltd., Japan). Mass spectra were measured on JEOL JNS-GCmate GCMS system (JEOL Ltd., Japan). Infrared spectra were measured on a PerkinElmer spectrum GX FT-IR system (PerkinElmer Japan Co. Ltd., Japan). Melting points were determined on a Yamato MP-21 Melting point apparatus (Yamato Scientific Co., Japan). Elemental analysis was performed by PerkinElmer 240-C.

### *Synthesis of Partially Unsaturated Thiacrown Ethers*

To an acetonitrile solution (300 mL) of disodium *cis*-ethenedithiolate [25,26] (2.59 g, 19.0 mmol), 3-bromo-1-propanol (7.22 g, 52.0 mmol) was added. The mixture was stirred for 3 h at room temperature. Resulting precipitates were filtered off, and the filtrate was concentrated under reduced pressure. Water was added to the residue, and products were extracted with dichloromethane. The combined solution was dried over sodium sulfate. After removal of the solvent in vacuo, purification by silica-gel column chromatography (ethyl acetate/hexane = 1/1) gave diol **1** (2.98 g, 75%). **1** [27]: $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 1. 52 (br, 2H), 1.97 (quint, $J$ = 6.7 Hz, 4H), 2.85 (t, $J$ = 6.7 Hz, 4H), 3.77 (br, 4H), 6.12 (s, 2H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 30.4, 32.5, 60.4, 123.5. To a dichloromethane solution (25 mL) of **1** (1.04 g, 5.00 mmol), *p*-toluenesulfonyl chloride (3.60 g, 18.9 mmol) and triethylamine (2.53 g, 24.7 mmol) were added. After stirring for 1 day at room temperature, saturated ammonium chloride solution was added to the mixture and the products were extracted with dichloromethane. The combined solution was dried over sodium sulfate. After removal of the solvent in vacuo, purification by silica-gel column chromatography (ethyl acetate/hexane = 1/5) gave ditosylate **2** (1.89 g, 73%). **2**: pale yellow liquid; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.95 (quint, $J$ = 6.3 Hz, 4H), 2.46 (s, 6H), 2.72 (t, $J$ = 6.3 Hz, 4H), 4.14 (t, $J$ = 6.3 Hz, 4H), 5.96 (s, 2H), 7.35 (d, $J$ = 8.8 Hz, 4H), 7.81 (d, $J$ = 8.8 Hz, 4H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 21.4, 29.3, 29.6, 68.1, 123.6, 127.6, 129.7, 132.6, 144.7; MS (EI) *m/z* 515 (M$^+$−1), 270, 172, 154; IR (liquid film) $\nu_{\max}$ 3359, 2924, 1919, 1598, 1360, 1175, 989, 815, 736, 664 cm$^{-1}$. Anal. Calcd for $C_{22}H_{28}O_6S_4$: C, 51.14; H, 5.46. Found: C, 51.04; H, 5.60. A DMF solution (25 mL) of disodium *cis*-ethenedithiolate (102 mg, 0.75 mmol), ditosylate **2** (258 mg, 0.50 mmol), and desired additive (0.10 mmol) was stirred for 4 h at room temperature. The reaction was quenched with 1 M hydrochloric acid solution, and the products were extracted with dichloromethane and ethyl acetate. The combined solution was dried over sodium sulfate. After removal of the solvent in vacuo, purification by silica-gel column chromatography (ethyl acetate/hexane = 1/30) afforded (*Z,Z*)-3,7,10,14-tetrathiacyclotetradeca-1,8-diene (**3**) and (*Z,Z,Z,Z*)-3,7,10,14,17,21,24,28-octathiacyclooctacosa-1,8,15,22-tetraene (**4**). **3** [11]:

$^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.95 (quint, $J = 6.7$ Hz, 4H), 2.86 (t, $J = 6.7$ Hz, 8H), 6.28 (s, 4H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 30.6, 32.5, 127.9; MS (EI) $m/z$ 264 (M$^+$), 158, 132; IR (KBr) $\nu_{\max}$ 2924, 2373, 1542, 1272, 1246, 729 cm$^{-1}$. **4:** Mp 105°C (decomp, colorless prisms from dichloromethane/hexane); $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.95 (quint, $J = 6.7$ Hz, 8H), 2.84 (t, $J = 6.7$ Hz, 16H), 6.17 (s, 8H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 30.8, 32.4, 124.5; MS (EI) $m/z$ 528 (M$^+$), 396, 277; IR (KBr) $\nu_{\max}$ 2918, 2372, 1542, 1290, 1252, 832, 727, 648 cm$^{-1}$. Anal. Calcd for $C_{20}H_{32}S_8$: C, 45.41; H, 6.10. Found: C, 45.61; H, 6.44.

### *Cyclic Voltammetry*

Cyclic voltammograms were measured in acetonitrile. A 0.1 M solution of tetra-*n*-butylammonium perchlorate was used as a supporting electrolyte solution. The samples were added and dissolved in this solution to yield 0.5 mM concentrations of the respective materials. Cyclic voltammograms were recorded at a scan rate of 100 mVs$^{-1}$. Formal oxidation potentials are given versus the reference system ferrocene/ferrocenium (Fc/Fc$^+$) in volts.

### *Thermal Isomerization of Partially Unsaturated Thiacrown Ethers*

DMSO-$d_6$ solution (0.4 mL) of partially unsaturated thiacrown ether **3** or **4** (ca. 10 mg) was heated at 140°C in an NMR tube. The reaction was monitored by $^{1}$H NMR measurements. Trace amounts of the *Z-E*-isomerized products, (*E,Z*)-3,7,10,14-tetrathiacyclotetradeca-1,8-diene **7**, and (*E,E*)-3,7,10,14-tetrathiacyclotetradeca-1,8-diene **8** were separated from the reaction mixture of **3** by silica-gel preparative thin layer chromatography (TLC; ethyl acetate/hexane = 1/20), and (*E,Z,Z,Z*)-3,7,10,14,17,21,24,28-octathiacyclooctacosa-1,8,15,22-tetraene (**10**) from **4** by pTLC (ethyl acetate/hexane = 1/50). **7**: $^{1}$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.95 (tt, $J = 8.1$, 5.6 Hz, 4H), 2.73 (t, $J = 5.6$ Hz, 4H), 2.87 (t, $J = 8.1$ Hz, 4H), 5.97 (s, 2H), 6.18 (s, 2H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 29.7, 31.2, 34.1, 118.7, 127.3; MS (EI) $m/z$ 264 (M$^+$), 158, 132. **8**: $^{1}$H NMR (270 MHz, CDCl$_3$) $\delta$ 1.94 (quint, $J = 7.5$ Hz, 4H), 2.73 (t, $J = 7.5$ Hz, 8H), 6.18 (s, 4H); $^{13}$C NMR (67.5 MHz, CDCl$_3$) $\delta$ 29.6, 31.3, 125.1; MS (EI) $m/z$ 264 (M$^+$), 158, 132. **10**: $^{1}$H NMR (500 MHz, CDCl$_3$) $\delta$ 1.92–1.98 (m, 8H), 2.77–2.87 (m, 16H), 6.11 (d, $J = 8.6$ Hz, 2H), 6.13 (s, 2H), 6.14 (s, 2H), 6.14 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 30.1, 30.9, 31.5, 32.47, 32.54, 32.7, 122.8, 124.0, 124.3, 124.7.

### *Theoretical Study*

The molecular structures for the model molecules and the 14-membered partially unsaturated thiacrown ethers were optimized by B3LYP/6-31G+(d,p), and the final energies were calculated by MP2/6-31G+(d,p) for the optimized structures.

### *Titration Experiment (Job's Plot)*

An acetone-$d_6$ solution (4 mM) of the partially unsaturated thiacrown ethers and an acetone-$d_6$ solution (4 mM) of the salts were mixed in various ratios to give total 0.5 mL of solution. The solutions were used for $^{1}$H NMR measurements.

### *Complexation with Mercury(II) Chloride*

To an acetonitrile solution (3 mL) of **3** (5.37 mg, 0.02 mmol), an acetonitrile solution (1 mL) of mercury (II) chloride (10.9 mg, 0.02 mmol) was added. The solution was stirred at room temperature for 2 h. Slow evaporation of the solvent afforded 1:2 complex **11** (7.77 mg, 48%). **11**: Mp 112°C (decomp, colorless prisms); $^{1}$H NMR (270 MHz, DMSO-$d_6$) $\delta$ 1.81 (quint, $J = 6.8$ Hz, 4H), 2.85 (t, $J = 6.8$ Hz, 8H), 6.37 (s, 4H). The structure was finally determined by X-ray analysis.

### *Crystal Data*

**4**: Compound **4** crystallized in the triclinic space group $P$-1,with $a = 5.235(9)$, $b = 10.422(19)$, $c = 12.33(2)$ Å, $\alpha = 104.39(2)$, $\beta = 93.69(2)$, $\gamma = 100.46°(2)$, $V = 636.2(19)$ Å$^3$, $Z = 2$, and $Dc = 1.380$ g cm$^{-3}$. 2788 data collected with Mo Ka radiation ($\lambda = 0.71070$ Å), and $Fo > 2.0\sigma(I)$ were used in the least-squares refinement to yield $R = 0.0522$, $R_w = 0.1246$. **7**: Compound **7** crystallized in the monoclinic space group $P21/n$, with $a = 9.988(4)$, $b = 8.868(3)$, $c = 14.570(5)$ Å, $\beta = 98.230°(4)$, $V = 1277.1(8)$ Å$^3$, $Z = 4$, and $Dc = 1.375$ g cm$^{-3}$. 2894 data collected with Mo Ka radiation ($\lambda = 0.71070$ Å), and $Fo > 2.0\sigma$(I) were used in the least-squares refinement to yield $R = 0.0651$, $R_w = 0.1887$. **11**: Complex **11** crystallized in the monoclinic space group $C2/c$, with $a = 14.384(8)$, $b = 9.957(6)$, $c = 13.344(7)$ Å, $\beta = 93.250°(7)$, $V = 1908.1(18)$ Å$^3$, $Z = 2$, and $Dc = 2.811$ g cm$^{-3}$. 2112 data collected with Mo Ka radiation $\lambda = 0.71070$ Å), and $Fo > 2.0\sigma(I)$ were used in the least-squares refinement to yield $R = 0.0290$, $R_w = 0.0637$.

## *SUPPLEMENTARY DATA*

Further details of crystal structure determination can be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223-336033; e-mail: deposit@ccdc.cam.ac.uk) on request. Deposition numbers CCDC 791514 (**4**), CCDC 790569 (**7**), and CCDC 791959 (**11**).

## *ACKNOWLEDGMENT*

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