

Macrocyclic Compounds Having Sulfide Moieties Derived from *o*-Terphenyl

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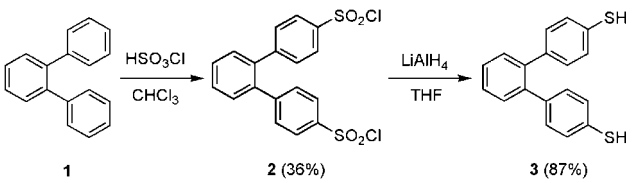
4,4″-Dimercapto-*o*-terphenyl as a precursor of macrocyclic compounds was prepared from *o*-terphenyl by chlorosulfonation and reduction. Eight macrocycles having sulfide moieties were synthesized from 4,4″-dimercapto-*o*-terphenyl. The thioethynyl compound, derived from 4,4″-dimercapto-*o*-terphenyl by introduction vinyl group and by addition of Br_2 following dehydrobromination, gave a novel cumulene upon treatment with cupric acetate in THF/pyridine. The structures of macrocyclic products were determined by ^1H and ^{13}C NMR, IR, and mass spectroscopies, elemental analysis, and X-ray crystallographic analysis. UV–vis and fluorescence spectra, and cyclic voltammogram, were also acquired.

Since cyclophanes are very important compounds in the fields of macrocyclic and supramolecular chemistry, there have been many reports concerning synthetic methodology and the chemical and physical properties.[1] Chemists in the field of material science are interested in specific structural, electrochemical, photophysical properties of cyclophanes, related polyaromatics, and polyphenylenes.[2,3] On the other hand, polyaromatics, cyclophanes, and polyphenylenes containing heteroatoms, e.g., oxygen,[4] nitrogen,[5,6] and sulfur,[7] as linkers have been also studied in terms of specific physical properties.

Many cyclophanes are often synthesized by desulfurization of the corresponding cyclophanes containing sulfur atoms.[1] Our recent interest has been directed to the study of the reactivity of polyphenylene compounds having a sulfide moiety. We selected *o*-terphenyl as a starting compound for synthesis of macrocyclic compounds, because it is well known that *o*-terphenyl easily forms macrocyclic compounds.[6] In fact, we succeeded in synthesizing many macrocyclic compounds having sulfide moieties from *o*-terphenyl. The thiolation of *o*-terphenyl was achieved by chlorosulfonylation with chlorosulfonic acid, followed by reduction with lithium aluminium hydride, to give 4,4″-dimercapto-*o*-terphenyl effectively. Treatment of 4,4″-dimercapto-*o*-terphenyl with oxidizing agents or some linkers, such as alkyl halide and acetylene derivatives, gave eight macrocycles. In particular, we synthesized a novel cumulene by the reaction of 4,4″-diethynylthio-*o*-terphenyl with cupric acetate. Here, we report the synthesis, structure, and photo- and electrochemical properties of new types of macrocycles derived from *o*-terphenyl.

Results and Discussion

Synthesis of 4,4″-Dimercapto-*o*-terphenyl and Oxidation Reaction. 4,4″-Dimercapto-*o*-terphenyl (**3**) was easily synthesized from commercially available *o*-terphenyl (**1**), which is a precursor of macrocycles by chlorosulfonylation with chlorosulfonic acid followed by reduction using lithium aluminium hydride as shown in Scheme 1.



1 **2** (36%) **3** (87%)

Scheme 1. Preparation of dithiol as precursor of macrocycles.

For cyclization, at first, we oxidized dithiol **3** using iodine and triethylamine in chloroform, which afforded easily cyclic disulfide **4** as the sole product in excellent yield (Scheme 2). Interestingly, we found that this reaction was independent of the reaction concentration, and thus it did not need to be performed in a dilute solution. It is well known that the synthesis of macrocycles requires dilute conditions because the ratio of oligomers, such as dimers, trimers, and oligomers, increases with an increase in reaction concentration. However, we carried out the oxidation of dithiol **3** using *N*-chlorosuccinimide (NCS) in a very dilute solution, and the results were the same as when other thiols were used. Thus, dimer-type **4**, trimer-type **5**, and an oligomer were formed as shown in Scheme 2. These results suggest that the use of a mild oxidizing reagent gave the oligomerization products, but a stronger one yielded only dimerization products.

Synthesis of Macrocycles Linked with Xylenyl Moiety. Cyclization of the dithiol using dichloroxylenes in the presence of K_2CO_3 in dilute condition afforded macrocycles **6**–**9** in moderate yields (Scheme 3). When dithiol **3** was reacted with *p*- and *m*-xylenyl dichlorides, we obtained macrocycles **6** and **7**, which consisted of one dithiol **3** and one dichloroxylene fragment. On the other hand, the use of *o*-xylenyl dichloride gave two macrocycles (**8** and **9**). Macrocycle **8** has two dithiol **3** and two *o*-xylenyl dichloride fragments, and macrocycle **9** is derived from two dithiol **3** and one *o*-xylenyl dichloride fragments. These results could be explained by the stability of these products based on the bond lengths and angles of the sulfur atom.

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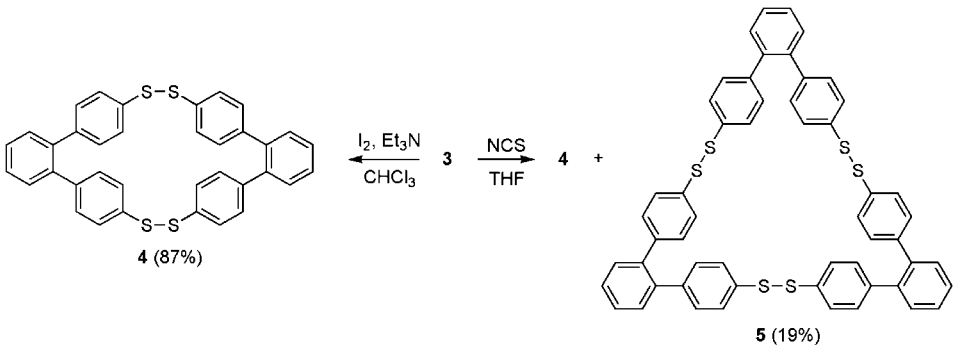
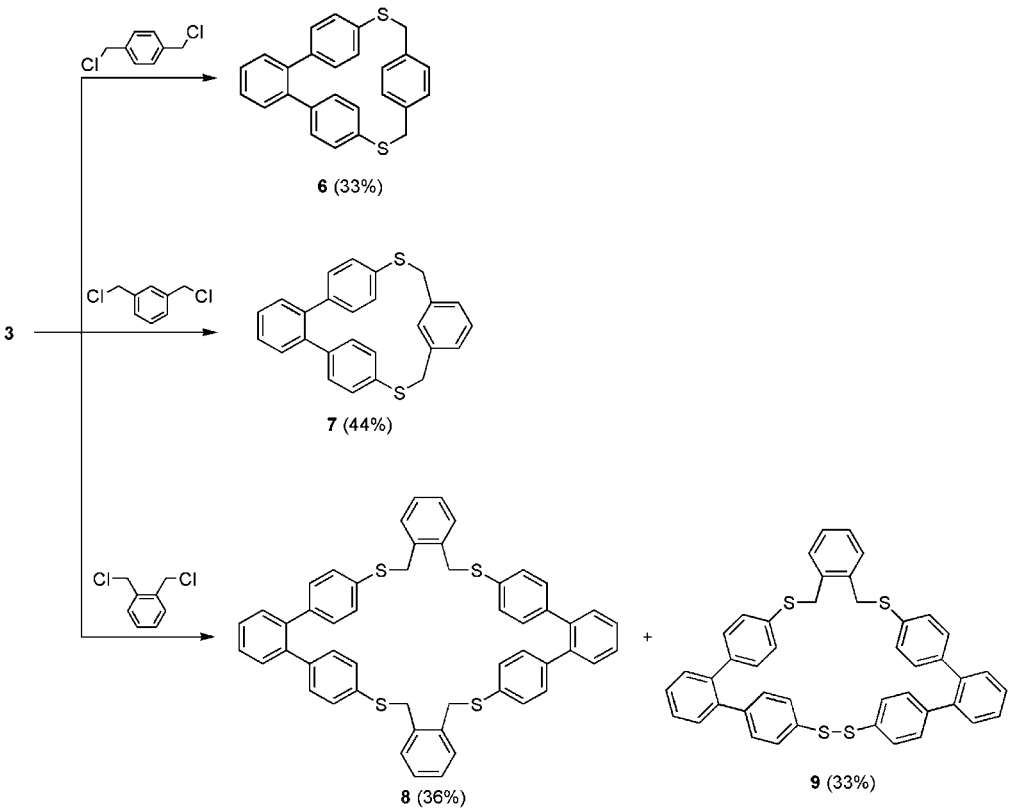


Scheme 2. Synthesis of macrocycles by oxidation of dithiol.



Scheme 3. Synthesis of macrocycles by introduction of xylene derivatives.

The structures of macrocycles **6**, **7**, and **9** were determined by X-ray crystallographic analysis. ORTEP views are shown in Figs. 1, 2 and 3, respectively, and selected bond lengths and angles, and torsion angles are shown in Table 1, 2, and 3, respectively. The bond lengths and angles of these macrocycles were normal for this type of molecule, and there was no distortion.

Synthesis of Macrocycles Containing Ethynyl Moieties. Two types of macrocycles **10** and **11** containing ethynyl moieties were synthesized in low yields by the reaction of dithiol **3** with acetylene lithium salt, which was prepared from bis(trimethylsilyl)acetylene by the treatment with methyl lithium (Scheme 4). This reaction seems to be competitive with the oxidation reaction to give dimer-type cyclic disulfide **4** and trimer-type cyclic disulfide **5**, and in fact, we obtained **4** and **5** in those reactions. We were able to synthesize of cyclic diyne **10** by another method. The reaction of thioethynyl derivative **13** with ^{n}BuLi and NCS gave the terminal chlorinated product, and further reaction with dithiol **3** in the presence of ^{n}BuLi in THF afforded cyclic diyne **10** in 20% yield as shown in Scheme 5. Thioethynyl derivative **13** was obtained by successive bromination and dehydrobromination of the corresponding vinyl derivative **12**, which was derived from dithiol **3** and vinyl bromide. Cyclic diyne **10** is made of two dithiol **3** and two acetylenyl moieties. Cyclic monoyne **11** is made of two dithiol **3** and one acetylenyl moiety.

The structure of cyclic diyne **10** was also determined by X-ray crystallographic analysis. An ORTEP view of **10** is shown in Fig. 4, and selected bond lengths, angles, and torsion angles are also listed in Table 4. Bond lengths were usual. Bond angle for C(2)–C(1)–S(1) was 169.82(19)°. Thus, the structure of **10** was slightly distorted. There is no report, to the best of our knowledge for the synthesis of this type compound, which contain an acetylenyl sulfide moeity, –S–C≡C–S–. Therefore,

compounds, **10** and **11** are the first examples of cyclophane containing a sulfur-capped ethynyl fragment.[8]

Next, we tried to synthesize a macrocyclic compound containing butadiyne unit as a linker by the Eglinton method[9] by using cupric acetate in THF/pyridine. However, we obtained a novel cumulene derivative **14** (Scheme 6).

The structure of cumulene **14** was determined by X-ray

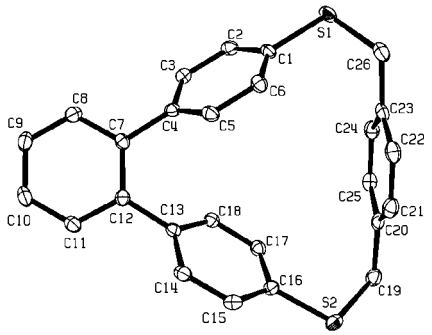


Fig. 1. ORTEP drawing of **6**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

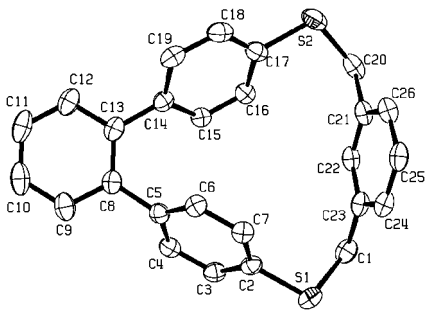


Fig. 2. ORTEP drawing of **7**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

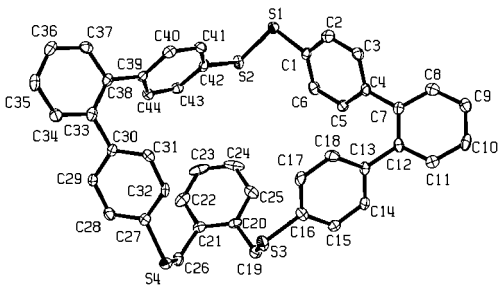


Fig. 3. ORTEP drawing of **9**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

Table 1. Selected Bond Lengths, Bond Angles, and Torsion Angles of **6**

Bond lengths/Å		Bond angles/°	
S(1)–C(1)	1.745(2)	C(26)–S(1)–C(1)	104.453(8)
S(1)–C(26)	1.827(2)	C(19)–S(2)–C(16)	102.50(8)
S(2)–C(16)	1.770(2)	S(1)–C(19)–C(20)	114.3(1)
S(2)–C(19)	1.778(2)	S(1)–C(26)–C(23)	114.3(1)
C(19)–C(20)	1.517(2)		
C(23)–C(26)	1.516(2)		

Torsion angles/°

C(3)–C(4)–C(7)–C(8)	−52.9(2)
C(11)–C(12)–C(13)–C(14)	−51.9(2)

Table 2. Selected Bond Lengths, Bond Angles, and Torsion Angles of **7**

Bond lengths/Å		Bond angles/°	
S(1)–C(1)	1.819(2)	C(2)–S(1)–C(1)	101.5(1)
S(1)–C(2)	1.779(3)	C(20)–S(2)–C(7)	103.7(1)
S(2)–C(17)	1.771(3)	S(1)–C(1)–C(23)	115.9(1)
S(2)–C(20)	1.820(2)	S(2)–C(20)–C(21)	115.3(1)
C(1)–C(23)	1.511(3)		
C(20)–C(21)	1.509(3)		

Torsion angles/°

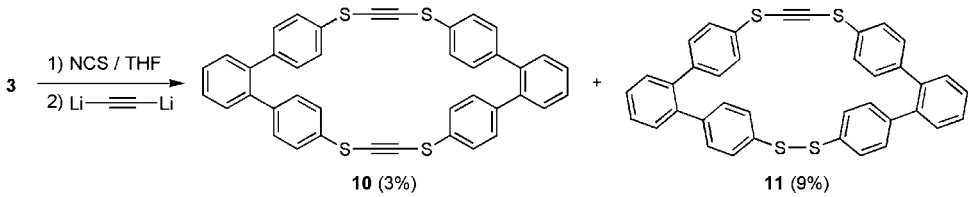
C(4)–C(5)–C(8)–C(9)	58.4(2)
C(12)–C(13)–C(14)–C(19)	48.7(3)

Table 3. Selected Bond Lengths, Bond Angles, and Torsion Angles of **9**

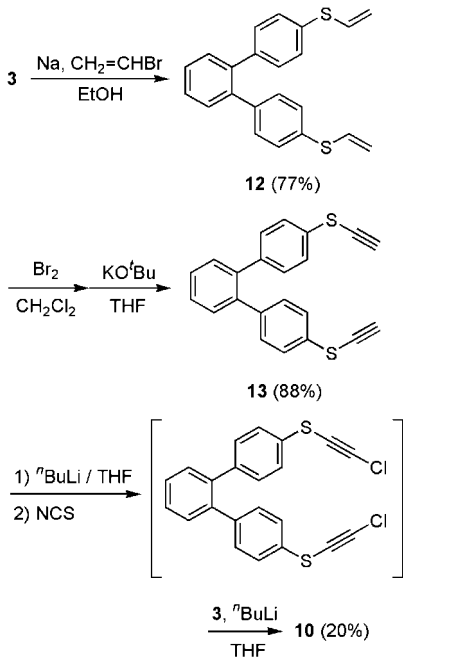
Bond lengths/Å		Bond angles/°	
S(1)–S(2)	2.0317(7)	C(1)–S(1)–S(2)	105.59(6)
S(1)–C(1)	1.785(2)	S(1)–S(2)–C(42)	106.83(7)
S(2)–C(42)	1.785(2)	S(1)–C(1)–C(2)	115.6(1)
S(3)–C(16)	1.781(2)	S(2)–C(42)–C(43)	114.1(2)
S(3)–C(19)	1.842(2)	S(3)–C(16)–C(17)	119.4(2)
S(4)–C(26)	1.839(2)	C(19)–S(3)–C(16)	102.0(1)
S(4)–C(27)	1.795(2)	S(3)–C(19)–C(20)	112.9(1)
C(19)–C(20)	1.494(3)	S(4)–C(26)–C(21)	113.1(1)
C(21)–C(26)	1.487(3)	C(27)–S(4)–C(26)	100.1(1)
		S(4)–C(27)–C(28)	120.5(2)

Torsion angles/°

C(3)–C(4)–C(7)–C(8)	47.4(3)
C(11)–C(12)–C(13)–C(14)	48.9(3)
C(29)–C(30)–C(33)–C(34)	−45.4(3)
C(37)–C(38)–C(39)–C(40)	−54.4(3)



Scheme 4. Synthesis of macrocycles by introduction of acetylene moiety.



Scheme 5. Synthesis of **10** by another method.

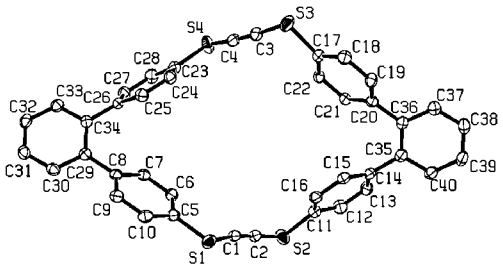


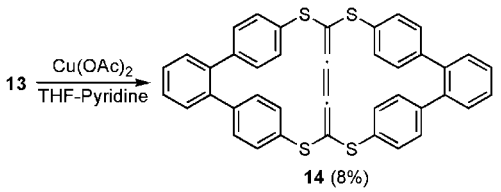
Fig. 4. ORTEP drawing of **10**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

Table 4. Selected Bond Lengths, Bond Angles, and Torsion Angles of **10**

Bond lengths/Å		Bond angles/°	
S(1)–C(1)	1.666(2)	C(1)–S(1)–C(5)	103.99(10)
S(1)–C(5)	1.7811(19)	C(2)–S(2)–C(11)	103.11(10)
S(2)–C(2)	1.673(2)	C(3)–S(3)–C(17)	104.19(10)
S(2)–C(11)	1.784(2)	C(4)–S(4)–C(23)	104.55(10)
S(3)–C(3)	1.669(2)	C(2)–C(1)–S(1)	169.82(19)
S(3)–C(17)	1.781(2)	C(1)–C(2)–S(2)	178.9(2)
S(4)–C(4)	1.655(2)	C(4)–C(3)–S(3)	176.2(2)
S(4)–C(23)	1.779(2)	C(3)–C(4)–S(4)	168.7(2)
C(1)–C(2)	1.207(3)		
C(3)–C(4)	1.212(3)		

Torsion angles/°

C(7)–C(8)–C(29)–C(30)	137.06(19)
C(25)–C(26)–C(34)–C(33)	122.0(2)
C(13)–C(14)–C(35)–C(40)	−50.4(3)
C(19)–C(20)–C(36)–C(37)	−40.7(3)



Scheme 6. Reaction of **13** by the Eglinton method.

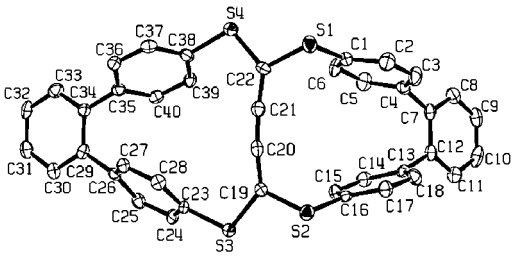


Fig. 5. ORTEP drawing of **14**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at the 50% probability.

Table 5. Selected Bond Lengths, Bond Angles, and Torsion Angles of **14**

Bond lengths/Å		Bond angles/°	
S(1)–C(22)	1.785(2)	S(1)–C(22)–C(21)	120.8(2)
S(2)–C(19)	1.784(2)	S(1)–C(22)–S(4)	108.04(9)
S(3)–C(19)	1.753(2)	S(2)–C(19)–C(20)	120.3(1)
S(4)–C(22)	1.745(2)	S(2)–C(19)–C(3)	108.4(1)
C(19)–C(20)	1.334(3)	S(3)–C(19)–S(20)	131.3(2)
C(20)–C(21)	1.279(3)	S(4)–C(22)–C(21)	131.0(2)
C(21)–C(22)	1.321(2)	C(19)–C(20)–C(21)	171.8(2)
C(1)–S(1)	1.773(3)	C(20)–C(21)–C(22)	174.1(2)
S(2)–C(16)	1.779(2)	C(22)–S(1)–C(1)	102.3(1)
S(3)–C(23)	1.770(2)	C(19)–S(2)–C(16)	101.7(1)
S(4)–C(38)	1.779(2)	C(23)–S(3)–C(19)	107.30(9)
		C(38)–S(4)–C(22)	104.97(9)

Torsion angles/°

C(3)–C(4)–C(7)–C(8)	−96.9(3)
C(11)–C(12)–C(13)–C(14)	−92.8(3)
C(25)–C(26)–C(29)–C(30)	57.1(3)
C(33)–C(34)–C(35)–C(36)	68.5(3)

crystallographic analysis. An ORTEP view is shown in Fig. 5. The structure of cumulene moiety was not linear. The bond angles of the cumulene were 171.8(2) and 174.3(2)°, and the torsion angles C(3)–C(4)–C(7)–C(8) and C(11)–C(12)–C(13)–C(14) were near 90°. Thus, the structure of the cumulene was slightly distorted (Table 5). As above-mentioned, we have succeeded in the first synthesis of a macrocyclic compound including a cumulene moiety capped with sulfur atoms.[10]

Property of Macrocyclic Compounds. The UV–vis and fluorescence spectra of dithiol and related compounds were measured in CH_2Cl_2. These results are shown in Table 6.

The intensity of absorbance in UV–vis spectra for dimer-type cyclic disulfide **4** was two times greater than that of dithiol **3**, and the absorbance for trimer-type cyclic disulfide **5** was three times greater than that of dithiol **3**. These results

Table 6. Photophysical Properties in CH_2Cl_2

	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{em}/nm[a)]
3	260	14940	398
4	257	36170	280, 288(sh), 361, 373
5	257	64748	280, 288(sh), 361, 372
6	271	30717	400
7	260	19728	403
8	277	34136	402
9	269	48161	380, 404
10	271	55480	395
11	267	50499	397
13	265	27566	395
14	434	12960	499
	247	52500	383, 404, 427, 453

a) All compounds were excited at λ_{max}.

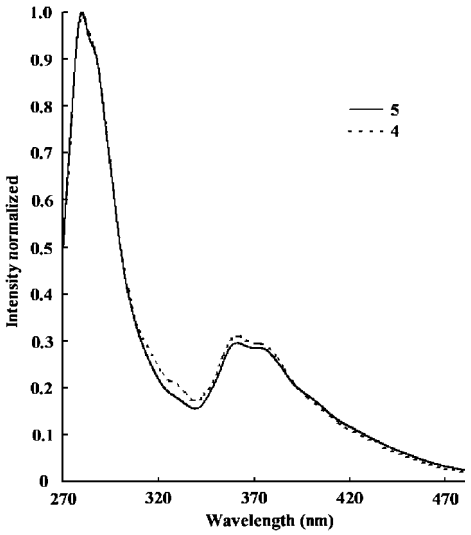


Fig. 6. Fluorescence spectra of dimer-type cyclic disulfide **4** and trimer-type cyclic disulfide **5** in CH_2Cl_2.

suggest that the additive properties of absorbance in UV–vis spectra are operative in the system, since these intensities of absorption depend on the number of dithiol units. The emission spectra of the oxidation products showed two specific pairs of peaks (Fig. 6). It means that structures are slightly distorted.

The UV–vis absorption and fluorescence spectra of **6–11** were similar. These results suggest that π-conjugation does not extend to the xylenyl moiety in **6–9** and the acetylenyl moiety at **10**, **11**, and these structures are not distorted in comparison to dithiol **3**. The data are consistent with the results from the X-ray crystallographic analyses.

In the case of the UV–vis spectrum of cumulene derivative **14**, two absorptions appeared. The peak at 247 nm, ascribed to the terphenyl moiety, was blue-shifted from that of dithiol, because torsion angles of the terphenyl moiety are larger than that of dithiol **3**. The peak at 434 nm was assigned to the cumulene moiety. The fluorescence spectrum of cumulene derivative **14** was fully assignable (Fig. 7), where as the spectrum excited by 247 nm was complex. The differences between peaks correspond to vibrational states, which was ca. 1350 cm^{-1}. The wavenumber attribute to the vibration of terphenyl moiety.

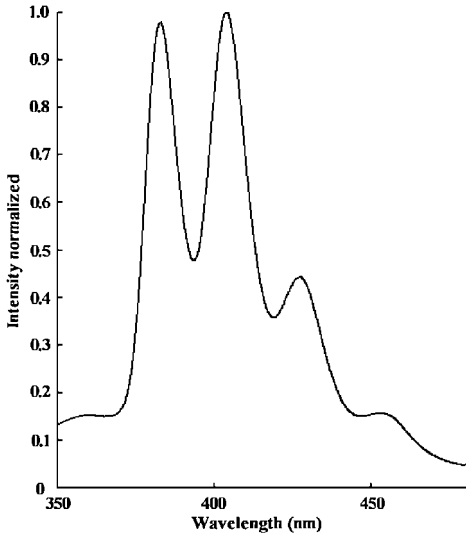


Fig. 7. Fluorescence spectrum of cumulene derivative **14** in CH_2Cl_2.

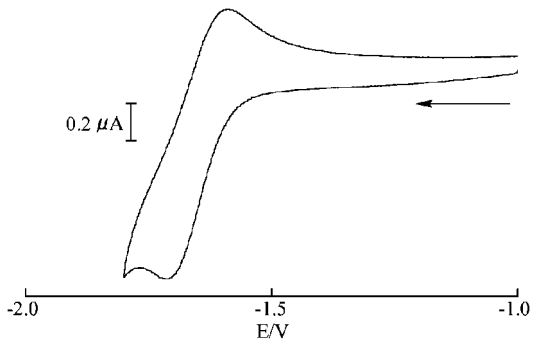


Fig. 8. Cyclic voltammogram of **14**.

Table 7. Redox Potentials [V] of **14**[a)]

E_{pc}	−1.69
E_{pa}	−1.59
$E_{1/2}$	−1.64

a) Concentration, 0.5 mM THF/0.1 M $^nBu_4NPF_6$; scan rate, 200 mV s^{-1}.

The cyclic voltammogram of cumulene **14**, in Fig. 8, was measured in THF containing 0.1 mol dm^{-3} of $^nBu_4NPF_6$ as a supporting electrolyte at room temperature under an argon atmosphere. All redox potentials are summarized in Table 7. Cumulene derivative **14** showed one reversible one-electron redox wave. This redox wave seems to be due to the cumulene moiety, suggesting that mono-anionic form (**14**$^{\bullet-}$) is relatively stable.

Conclusion

In conclusion, we synthesized new types of macrocycles containing sulfur. These structures were determined by X-ray crystallographic analysis. The UV–vis and fluorescence spectra of the macrocycles suggested that dimer-type cyclic disulfide **4**, trimer-type cyclic disulfide **5**, and cumulene derivative **14** were distorted in comparison to other macrocycles. In the cyclic voltammogram of cumulene derivative **14**, there was one reversible one-electron redox wave.

Experimental

General Procedure. Melting and decomposition points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H (400 MHz) and ^{13}C (101 MHz) NMR spectra were measured on a Bruker AC-400 spectrometer in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were recorded on a JASCO FT-7300 spectrometer. Mass spectra were determined on a Hitachi M-2000 spectrometer operating at 70 eV in the EI mode. Elemental analyses were carried out on a Yanagimoto MT-5 CHN corder. High-resolution mass spectra were obtained using an Applied Biosystems Japan QSTAR XL Hybrid LC/MS/MS System. The UV–vis spectra were measured on a JASCO V-570 UV–vis spectrometer in CH_2Cl_2 solution. Emission spectra were obtained using a JASCO FP-6500 spectrometer in CH_2Cl_2 solution. Cyclic voltammetry was carried out with a Cypress Systems CS-1090 galvanostat/potentiostat. A three electrode system, consisting of a glassy-carbon working electrode, a platinum wire auxiliary electrode, and Ag/0.01 M $AgNO_3$ reference electrode, was used. The measurements were carried out in THF solution containing 0.1 M Bu_4NPF_6 as a supporting electrolyte under argon atmosphere. All solvents used in the reactions purified by general methods. Silica-gel column chromatography was performed with Wakogel C-200.

4,4″-Dichlorosulfonyl[1,1′:2′,1″]terphenyl (2). To a solution of *o*-terphenyl (23.030 g, 100 mmol) in $CHCl_3$ (100 mL) at 0 °C was added chlorosulfonic acid (33 mL, 500 mmol). After stirring at room temperature for 72 h, the mixture was poured into ice water. The mixture was extracted with $CHCl_3$. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. The mixture was purified by chromatography on silica gel (ϕ = 5.0 cm, h = 10 cm, $CHCl_3$) to give 15.501 g (36%) of 4,4″-dichlorosulfonyl[1,1′:2′,1″]terphenyl (**2**) as a colorless crystals: mp 164–165 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, J = 8.5 Hz, 4H, ArH), 7.47–7.49 (m, 2H, ArH), 7.56–7.59 (m, 2H, ArH), 7.96 (d, J = 8.5 Hz, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.0, 129.3, 130.8, 130.9, 138.0, 142.8, 147.8; IR (KBr) 1375 (SO_2), 1173 (SO_2) cm^{-1}; MS (70 eV) m/z 426 (M^+); HR-APCI-MS Calcd for $C_{18}H_{13}Cl_2O_4S_2$ $[M + H]^+$: 426.9626. Found: 426.9641.

4,4″-Dimercapto[1,1′:2′,1″]terphenyl (3). To a solution of **2** (15.0 g, 35.1 mmol) in THF (200 mL) at 0 °C was added $LiAlH_4$ (13.3 g, 351 mmol). After stirring at reflux for 5 h, the mixture was poured into ice water, followed by the addition HCl aq until everything dissolved. The mixture was extracted with $CHCl_3$, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2, and extracted with 1 M NaOH aq. A conc. HCl aq was added to the water layer until pH <1. The mixture was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel (ϕ = 5.0 cm, h = 10 cm, $CHCl_3$) gave 9.196 g (89%) of 4,4″-dimercapto[1,1′:2′,1″]terphenyl (**3**) as a yellow crystals: mp 157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.40 (s, 2H, SH), 7.00 (d, J = 8.2 Hz, 4H, ArH), 7.13 (d, J = 8.2 Hz, 4H, ArH), 7.35–7.40 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.6, 128.9, 129.0, 130.4, 138.8, 139.5; IR (KBr) 2555 (SH) cm^{-1}; MS (70 eV) m/z 294 (M^+); Anal. Calcd for $C_{18}H_{14}S_2$: C, 73.43; H, 4.79%. Found: C, 73.23; H, 4.84%.

1,2,21,22-Tetrathia[2,2](4,4″)-*o*-terphenylophane (4). To a solution of **3** (1.472 g, 5 mmol) and triethylamine (1.4 mL, 10 mmol) in $CHCl_3$ (100 mL) was added iodine (1.269 g, 5 mmol). After stirring at room temperature for 20 h, $NaHSO_3$ aq was added. Then the mixture was stirred at room temperature for 1 h. The mixture was filtrated washed with $CHCl_3$. The residue was dried in vacuo to give 1.268 g (87%) of 1,2,21,22-tetrathia[2,2](4,4″)-*o*-terphenylophane (**4**) as a colorless solids: mp 250–251 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09–7.12 (m, 4H, ArH), 7.33–7.35 (m, 4H, ArH), 7.37–7.40 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.8, 130.5, 130.8, 136.1, 139.4; IR (KBr) 4489, 4347, 4297, 4209, 3853, 3675, 3613, 3368, 3019, 2355, 1592, 1469, 1393, 1079, 1001, 827, 759, 558 cm^{-1}; MS (70 eV) m/z 584 (M^+); Anal. Calcd for $C_{36}H_{24}S_4$: C, 73.93; H, 4.14%. Found: C, 73.61; H, 4.31%.

1,2,21,22,41,42-Hexathia[2,2,2](4,4″)-*o*-terphenylophane (5). Under the nitrogen atmosphere, a mixture of **3** (294 mg, 1 mmol) and NCS (294 mg, 2.2 mmol) at 0 °C was dissolved into THF (100 mL). After stirring at room temperature for 24 h, water was added. The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel (ϕ = 4.0 cm, h = 9.0 cm, $CHCl_3$/hexane (1:1 v/v)), followed by GPC gave 54 mg (19%) of 1,2,21,22,41,42-hexathia[2,2,2](4,4″)-*o*-terphenylophane (**5**) as a colorless solids: mp 175–176 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (d, J = 8.2 Hz, 12H, ArH), 7.24 (d, J = 8.2 Hz, 12H, ArH), 7.38–7.43 (m, 12H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 127.9, 128.5, 130.3, 130.5, 135.6, 139.7, 140.8; IR (KBr) 3017, 1590, 1489, 1470, 1439, 1395, 1061, 1004, 823, 760, 555, 481, 425 cm^{-1}; SIMS (70 eV) m/z 876 (M^+); Anal. Calcd for $C_{54}H_{36}S_6$: C, 73.93; H, 4.14%. Found: C, 73.72; H, 4.33%.

1,10-Dithia[2]paracyclo[2](4,4″)-*o*-terphenylophane (6). Under the nitrogen atmosphere, a mixture of **3** (294 mg, 1 mmol), K_2CO_3 (552 mg, 4 mmol), and α,α'-dichloro-*p*-xylene (175 mg, 1 mmol) was dissolved into THF (100 mL). After stirring at room temperature for 20 h, the mixture was poured into ice water, and conc. HCl aq was added until pH <1. The mixture was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel (ϕ = 3.5 cm, h = 8.0 cm, $CHCl_3$/hexane (1:1 v/v)) gave 130 mg (33%) of 1,10-dithia[2]paracyclo[2](4,4″)-*o*-terphenylophane (**6**) as a colorless needles: mp 225–226 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (s, 4H, CH_2), 6.70 (d, J = 8.2 Hz, 4H, ArH), 6.88 (d, J = 8.2 Hz, 4H, ArH), 7.20 (s, 4H, ArH), 7.30–7.35 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.2, 127.2, 128.9, 129.0, 129.3, 129.4, 131.9, 135.1, 138.6, 140.8; IR (KBr) 3053, 3021, 2939, 1595, 1505, 1471, 1430, 1395, 1242, 1192, 1154, 1094, 1017, 1000, 900, 872, 813, 757, 746, 713, 562, 519, 461, 443 cm^{-1}; MS (70 eV) m/z 396 (M^+); Anal. Calcd for $C_{26}H_{20}S_2$: C, 78.74; H, 5.08%. Found: C, 78.59; H, 5.15%.

1,10-Dithia[2]metacyclo[2](4,4″)-*o*-terphenylophane (7). Under the nitrogen atmosphere, a mixture of **3** (147 mg, 0.5 mmol), K_2CO_3 (276 mg, 2.0 mmol), and α,α'-dichloro-*m*-xylene (88 mg, 0.5 mmol) was dissolved into THF (100 mL). After stirring at room temperature for 78 h, the solution was poured into ice water, and conc. HCl aq was added until pH <1. The mixture was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel (ϕ = 3.5 cm, h = 8.0 cm, $CHCl_3$/hexane (1:1 v/v)) gave 81 mg (44%) of 1,10-dithia[2]metacyclo[2](4,4″)-*o*-terphenylophane (**7**) as a colorless blocks: mp 229–230 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (s, 4H, CH_2), 6.63 (br s, 1H, ArH), 6.76 (d, J = 8.2 Hz, 4H, ArH), 7.02 (d, J = 8.2 Hz, 4H, ArH), 7.33–7.37 (m, 1H, ArH), 7.39 (m, 4H, ArH), 7.44–7.48 (m, 2H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 38.7, 127.5, 127.6, 128.8, 128.9, 130.1, 131.2, 131.3, 131.4, 137.4, 140.1, 140.9; IR (KBr) 3056, 2898, 1598, 1467, 1442, 1404, 1221,

1094, 1000, 904, 830, 773, 704, 565, 520, 434 cm^{-1}; MS (70 eV) m/z 396 (M^+); Anal. Calcd for $C_{26}H_{20}S_2$: C, 78.74; H, 5.08%. Found: C, 78.90; H, 5.14%.

1,10,29,38-Tetrathia[2]orthocyclo[2](4,4″)-*o*-terphenylo[2]-orthocyclo[2](4,4″)-*o*-terphenylophane (8) and 1,10,29,30-Tetrathia[2]orthocyclo[2.2](4,4″)-*o*-terphenylophane (9). Under the nitrogen atmosphere, a mixture of **3** (294 mg, 1 mmol), K_2CO_3 (552 mg, 4 mmol), and α,α'-dichloro-*o*-xylene (175 mg, 1 mmol) was dissolved into THF (100 mL). After stirring at room temperature for 20 h, the solution was poured into ice water, and conc. HCl aq was added until pH <1. The mixture was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel ($\phi = 3.5$ cm, $h = 8.0$ cm, $CHCl_3$/hexane (1:1 v/v)) 141 mg (36%) of 1,10,29,38-tetrathia[2]orthocyclo[2](4,4″)-*o*-terphenylo-[2]orthocyclo[2](4,4″)-*o*-terphenylophane (**8**) as a colorless crystals and gave 115 mg (33%) of 1,10,29,30-tetrathia[2]orthocyclo-[2.2](4,4″)-*o*-terphenylophane (**9**) as a colorless crystals. **8**: Colorless crystals: mp 290–291 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (s, 8H, CH_2), 6.98 (d, $J = 8.2$ Hz, 8H, ArH), 7.10 (d, $J = 8.2$ Hz, 8H, ArH), 7.17 (s, 8H, ArH), 7.34–7.40 (m, 8H, ArH); IR (KBr) 3061, 3020, 1594, 1490, 1469, 1454, 1389, 1237, 1185, 1090, 1019, 1003, 947, 819, 762, 730, 562, 521, 481, 464 cm^{-1}; HR-APCI-TOF-MS Calcd for $C_{52}H_{41}S_4$ $[M + H]^+$: 793.2085. Found: 793.2076; Anal. Calcd for $C_{52}H_{40}S_4$: C, 78.74; H, 5.08%. Found: C, 78.50; H, 5.33%. **9**: Colorless blocks: mp 226–227 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 (s, 4H, CH_2), 7.04 (d, $J = 8.2$ Hz, 4H, ArH), 7.09 (d, $J = 8.3$ Hz, 4H, ArH), 7.15 (d, $J = 8.2$ Hz, 4H, ArH), 7.210–7.213 (m, 4H, ArH), 7.35 (d, $J = 8.3$ Hz, 4H, ArH), 7.37–7.42 (m, 8H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 36.6, 127.7, 127.80, 127.88, 129.5, 129.9, 130.3, 130.4, 130.6, 130.7, 134.5, 135.3, 135.5, 139.3, 139.5, 139.6, 141.2; IR (KBr) 3051, 3019, 2926, 1901, 1655, 1594, 1490, 1470, 1440, 1387, 1236, 1215, 1183, 1091, 1078, 1017, 1004, 880, 830, 771, 760, 677, 634, 599, 565, 517, 467, 432 cm^{-1}; SIMS (70 eV) m/z 689 ($M^+ + 1$); HR-APCI-TOF-MS Calcd for $C_{44}H_{33}S_4$ $[M + H]^+$: 689.1459, found: 689.1485; Anal. Calcd for $C_{44}H_{32}S_4$: C, 76.70; H, 4.68%. Found: C, 76.44; H, 4.66%.

4,4″-Bisvinylsulfanyl[1,1′;2′,1″]terphenyl (12). To a solution of **3** (3.533 g, 12 mmol) and diphenylamine (80 mg) as polymerization retardant in EtOH (30 mL) at 0 °C was added sodium (0.827 g, 36 mmol) and vinylbromide (2.8 mL, 36 mmol). After stirring at 120 °C for 40 h, the solution was filtered. The solvent was evaporated, and the residue was dissolved in Et_2O. The solution was washed with water and dried over $MgSO_4$. The mixture obtained by evaporation was purified by chromatography on silica gel ($\phi = 3.2$ cm, $h = 27.5$ cm, $CHCl_3$/hexane (1:1 v/v)), to give 3.195 g (77%) of 4,4″-bisvinylsulfanyl[1,1′;2′,1″]terphenyl (**12**) as a colorless crystals: mp 119–120 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (d, $J = 16.7$ Hz, 2H, SCH=CH_2), 5.35 (d, $J = 9.4$ Hz, 2H, SCH=CH_2), 6.52 (dd, $J = 9.4$ Hz, 16.7 Hz, 2H, SCH=CH_2), 7.09 (d, $J = 8.3$ Hz, 4H, ArH), 7.23 (d, $J = 8.3$ Hz, 4H, ArH), 7.40–7.42 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 115.5, 127.7, 129.8, 130.4, 130.5, 131.6, 132.5, 139.6, 140.2; IR (KBr) 3018, 1655, 1584, 1491, 1467, 1440, 1398, 1372, 1093, 1003, 949, 882, 824, 764, 730, 586, 556, 521, 488, 420 cm^{-1}; MS (70 eV) m/z 346 (M^+); Anal. Calcd for $C_{22}H_{18}S_2$: C, 76.26; H, 5.24%. Found: C, 76.21; H, 5.46%.

4,4″-Bisethynylsulfanyl[1,1′;2′,1″]terphenyl (13). To a solution of **12** (3.195 mg, 9.22 mmol) in methylene dichloride (40 mL) at 0 °C was added a bromine methylene dichloride solution (92 mL, 0.2 M, 18.4 mmol). Then, the mixture was treated with $NaHSO_3$ aq and extracted with methylene dichloride. The organic layer was dried over $MgSO_4$ and filtered. The solvent was evaporated. The residue was dissolved in THF (50 mL). Potassium *t*-butoxide (4.138 g, 36.9 mmol) was added to the solution at 0 °C. After the mixture was stirred at reflux for 16 h, the mixture was filtered, and the filtrate extracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel ($\phi = 3.2$ cm, $h = 20.0$ cm, $CHCl_3$/hexane (1:1 v/v)) gave 2.890 g (92%) of 4,4″-bisethynylsulfanyl[1,1′;2′,1″]terphenyl (**13**) as a pale yellow crystals: mp 102–103 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 2H, SCCH), 7.10 (d, $J = 8.4$ Hz, 4H, ArH), 7.30 (d, $J = 8.4$ Hz, 4H, ArH), 7.36–7.42 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 70.7, 87.1, 126.0, 127.8, 129.8, 130.5, 130.6, 139.3, 139.8; IR (KBr) 3270 (CCH), 2044 cm^{-1}; MS (70 eV) m/z 342 (M^+); Anal. Calcd for $C_{22}H_{14}S_2$: C, 77.15; H, 4.12%. Found: C, 77.19; H, 4.22%.

1,4,23,26-Tetrathia[4.4](4,4″)-*o*-terphenylophane-2,24-yne (10) and 1,4,23,24-Tetrathia[4.2](4,4″)-*o*-terphenylophane-2-yne (11). Under the nitrogen atmosphere, a mixture of **3** (294 mg, 1 mmol) and NCS (280 mg, 2.1 mmol) at 0 °C was dissolved into anhydrous THF (80 mL). The solution was stirred at r.t. for 1 h. To this solution, a solution of bistrimethylsilyl acetylene (0.47 mL, 2.1 mmol) in anhydrous THF (20 mL) and MeLi (3.9 mL, 4.2 mmol, 1.08 M solution in diethyl ether) were added at 0 °C. After stirring at r.t. for 15 h, water and then dilute HCl aq were added until ca. pH 3. The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel ($\phi = 3.2$ cm, $h = 19.0$ cm, $CHCl_3$/hexane (1:1 v/v)), followed by GPC gave 9 mg (3%) of 1,4,23,26-tetrathia[4.4](4,4″)-*o*-terphenylophane-2,24-yne (**10**) as a colorless crystals and 27 mg (9%) of 1,4,23,24-tetrathia[4.2](4,4″)-*o*-terphenylophane-2-yne (**11**) as a colorless crystals. **10**: Colorless crystals; mp >300 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (d, $J = 8.4$ Hz, 8H, ArH), 7.30 (d, $J = 8.4$ Hz, 8H, ArH), 7.36–7.42 (m, 8H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.2, 125.3, 127.8, 130.7, 130.9, 131.7, 136.5, 139.3; IR (KBr) 3058, 3021, 1593, 1491, 1470, 1440, 1395, 1219, 1185, 1104, 1085, 1016, 1002, 825, 755, 668, 554, 523 cm^{-1}; SIMS (70 eV) m/z 632 (M^+); Anal. Calcd for $C_{40}H_{24}S_4$: C, 75.91; H, 3.82%. Found: C, 75.78; H, 4.10%. **11**: Colorless crystals; mp 238–239 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, $J = 8.3$ Hz, 4H, ArH), 7.20 (d, $J = 8.4$ Hz, 4H, ArH), 7.30 (d, $J = 8.4$ Hz, 4H, ArH), 7.34–7.42 (m, 8H, ArH), 7.42 (d, $J = 8.3$ Hz, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.5, 125.1, 125.9, 127.7, 127.8, 130.4, 130.7, 130.8, 131.2, 131.7, 135.2, 139.0, 139.2, 139.8, 140.0; IR (KBr) 3054, 3017, 1590, 1489, 1469, 1440, 1395, 1215, 1083, 1016, 1000, 827, 761, 668, 555, 525 cm^{-1}; SIMS (70 eV) m/z 608 (M^+); Anal. Calcd for $C_{38}H_{24}S_4$: C, 74.96; H, 3.97%. Found: C, 74.72; H, 4.08%.

1,4,23,26-Tetrathia[4.4](4,4″)-*o*-terphenylophane-2,24-yne (10) (Another Method). Under a nitrogen atmosphere, to a solution of **13** (171 mg, 0.5 mmol) in anhydrous THF (5 mL) at −30 °C was added ^{n}BuLi (0.71 mL, 1.1 mmol, 1.54 M solution in pentane). After stirring at −30 °C for 0.5 h, anhydrous THF solution (5 mL) of NCS (140 mg, 1.05 mmol) added at −30 °C. After stirring at r.t. for 0.5 h, water added. The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated to afford terminated chlorination product (**A**). Under the nitrogen atmosphere, to a solution of **3** (147 mg, 0.5 mmol) in anhydrous THF (50 mL) at 0 °C was added ^{n}BuLi (0.68 mL, 1.05 mmol, 1.54 M solution in pentane). After stirring at 0 °C for 0.5 h, anhydrous THF solution (50 mL) of **A**

Table 8. Crystallographic Data and Experimental Parameters for the Crystal Structure Analysis of Macrocycles **6**, **7**, **9**, **10**, and **14**

	6	**7**	**9**	**10**	**14**
Empirical formula	$C_{26}H_{20}S_2$	$C_{26}H_{20}S_2$	$C_{44}H_{32}S_4$	$C_{40}H_{24}S_4$	$C_{40}H_{24}S_4$
Formula weight	395.56	395.56	688.98	632.87	632.87
Crystal dimensions/mm^3	0.20 × 0.20 × 0.10	0.40 × 0.80 × 0.40	0.20 × 0.15 × 0.40	0.50 × 0.35 × 0.20	0.10 × 0.06 × 0.30
Collection temperature/K	103	103	103	103	103
Crystal system	monoclinic	monoclinic	orthorhombic	monoclinic	triclinic
a/Å	9.718(4)	13.45(5)	7.986(2)	12.125(3)	9.6301(6)
b/Å	19.365(8)	16.45(6)	17.858(3)	13.195(2)	10.0109(8)
c/Å	10.420(4)	13.56(5)	24.430(5)	13.850(3)	16.584(1)
α/deg	90	90	90	67.336(8)	102.139(3)
β/deg	91.38(3)	138.0(2)	90	86.992(6)	98.387(4)
γ/deg	90	90	90	77.905(11)	97.371(3)
V/Å^3	1960(1)	2006(11)	3484(1)	1998.5(7)	1525.3(2)
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	$P2_12_12_1$ (#19)	$P\bar{1}$ (#2)	$P\bar{1}$ (#2)
Z value	4	4	4	2	2
μ (Mo Kα)/cm^{-1}	2.81	2.74	3.05	2.73	3.41
D_{calcd}/g cm^{-3}	1.344	1.313	1.313	1.275	1.378
No. of indep reflns	4472	4584	7928	7025	6805
No. of params	334	333	563	536	493
R_1	0.036	0.042	0.030	0.0383	0.042
wR_2	0.079	0.113	0.031	0.0953	0.039
GOF	1.012	1.001	1.000	0.991	0.994

slowly added over 0.5 h to keep the temperature at 0 °C. After stirring at r.t. for 24 h, water and then dilute HCl aq were added until ca. pH 3. The mixture was extracted with Et_2O. The organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel ($\phi = 3.2$ cm, $h = 12.0$ cm, $CHCl_3$/hexane (1:1 v/v)) gave 63 mg (20%) of 1,4,23,26-tetrathia[4.4](4,4″)-*o*-terphenylophane-2,24-yne (**10**) as a colorless crystals.

2,23-(Ethene-1,2-diylidene)-1,3,22,24-tetrathia[3.3](4,4″)-*o*-terphenylophane (14). Under a nitrogen atmosphere, **13** (0.114 g, 0.333 mmol) dissolved THF/pyridine (50 mL) (1:1 v/v) was added dropwise into a solution of cupric acetate (0.400 g, 2.20 mmol) in THF–pyridine (50 mL) (1:1 v/v) for over 12 h to keep the temperature at 80 °C. After stirring at 80 °C for 24 h, the mixture was poured into dilute HCl aq at 0 °C. The mixture was extracted with $CHCl_3$, and the organic layer was dried over $MgSO_4$ and filtered, and the solvent was evaporated. Chromatography on silica gel ($\phi = 2.0$ cm, $h = 11.0$ cm, $CHCl_3$/hexane (1:1 v/v)), followed by GPC gave 8 mg (8%) of 2,23-(ethene-1,2-diylidene)-1,3,22,24-tetrathia[3.3](4,4″)-*o*-terphenylophane (**14**) as a yellow plates: mp >300 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.79 (d, $J = 8.2$ Hz, 8H, ArH), 7.14 (d, $J = 8.2$ Hz, 8H, ArH), 7.45–7.49 (m, 4H, ArH), 7.50–7.53 (m, 4H, ArH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 111.7, 127.3, 127.6, 128.9, 130.8, 133.8, 141.2, 142.2, 150.7; IR (KBr) 3053, 3020, 2924, 1989 (C=C=C), 1590, 1542, 1498, 1464, 1392, 1178. 1088, 1017, 1001, 828, 758, 717, 676, 568, 513, 437 cm^{-1}; HR-APCI-MS Calcd for $C_{40}H_{25}S_4$ $[M + H]^+$: 633.0833. Found: 633.0812.

X-ray Crystallographic Analysis. Single crystals suitable for X-ray crystallographic analysis were obtained by slow evaporation of a $CHCl_3$/*n*-hexane solution of **6**, **7**, and **9**, a $CHCl_3$/toluene solution of **10**, and a $CHCl_3$ solution of **14** at room temperature. The intensity data were collected on a Rigaku R-AXIS RAPID diffractometer employing Mo Kα ($\lambda = 0.71705$ Å) radiation. For compounds **6**, **7**, and **9**, the structure solved by direct methods (SIR 97)[11] and expanded using Fourier technique (DIRDIF-99).[12] All calculations were performed using the Crystal Structure Rigaku/MSC. For compounds **10**, and **14**, the structure was solved by direct method (SHELXS-97)[13] and refined by full-matrix least-squares procedures in F^2 for all reflections (SHELXL-97).[14] For compound **10**, a toluene molecule was disordered at 8:2 and a 0.5 toluene does not displace the hydrogen atom. The all crystallographic data are summarized in Table 8.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition number CCDC-626433 for compound No. **6** and CCDC-626434 for compound No. **7** and CCDC-626435 for compound No. **9** and CCDC-626436 for compound No. **10** and CCDC-626437 for compound No. **14**. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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