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Selective oxidation of thiacalix[4]arenes to the sulfinyl and sulfonyl counterparts and their complexation abilities toward metal ions as studied by solvent extraction☆

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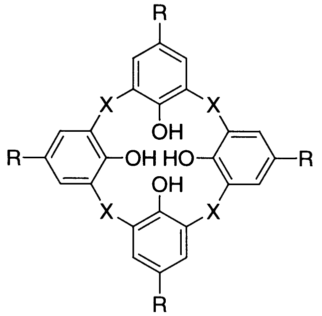
Abstract—Practical methods for the synthesis of sulfinyl-(**5**,**6**) and sulfonylcalix[4]arenes (**7**,**8**) were provided by the selective oxidation of thiacalix[4]arenes (**3**,**4**) with controlled amounts of an oxidant such as $NaBO_3$ or hydrogen peroxide under mild conditions. The coordination ability of thiacalix[4]arene **4** and the sulfinyl and sulfonyl analogs (**6**,**8**) toward a wide variety of metal ions was investigated by solvent extraction and compared to that of the conventional methylene-bridged calix[4]arene **2**. It was shown that the metal-ion selectivities of the sulfur-containing ligands **4**, **6**, and **8** were controlled by the oxidation state of the bridging sulfur moiety, which was best understood based on the hard and soft acid–base (HSAB) principle by assuming the critical role of the bridging groups in coordination to the metal center. Thus, **4** preferred soft metal ions by binding with S, while **8** did hard ones by ligating with sulfonyl O in addition to the adjacent two phenoxide oxygens, respectively. In good accordance with this hypothesis, **6** could bind to both hard and soft metal ions by using sulfinyl O and S, respectively. These made sharp contrast to the parent methylene-bridged **2**, which could not essentially extract any metal ions at all, lacking lone pair electrons on the methylene bridge for coordination. © 2001 Elsevier Science Ltd. All rights reserved.

1. Introduction

In molecular recognition and supramolecular chemistry, calixarenes (e.g. **1**, **2**, Scheme 1)[2] play unique roles as synthetic receptors.[3] For example, metal binding abilities of calixarene-based receptors have been successfully applied to extractants,[4] chromogenic sensors,[5] fluorometric sensors,[6] ionophores for ion-selective electrodes[7] and field effect transistors,[8] and luminescence labeling reagents.[9] Undoubtedly, these applications rely on the feasibility of the calixarene platform to be variously designed by introducing proper ligating functional groups via etherification of the phenolic oxygens (lower rim)[10] and/or substitution of the *p*-position (upper rim).[11] Replacement of the methylene bridges of the conventional calixarenes by hetero atoms should be an alternative resort to construct a calixarene-type receptor, which, however, has very rarely been practiced due to the synthetic difficulty. As one of such trials, Sone et al. first synthesized *p*-*tert*-butylthiacalix[4]arene (**3**) by acid catalyzed cyclization of an acyclic tetramer (4% yield).[12,13] König et al. synthesized *p*-*tert*-butylsilacalix[4]arene-tetramethyl ether, in which the linking units (X) are $Si(CH_3)_2$, by stepwise reaction of *p*-*tert*-butylmethoxybenzene and dichlorodimethylsilane followed by cyclization (13% yield).[14] However, these works were seemingly only limited to the synthesis and study on the physicochemical properties of the hetero-calixarenes themselves, as the synthetic difficulty may have had prevented their application to molecular receptors.

Recently, we reported a facile synthesis of **3** by base-catalyzed condensation of *p*-*tert*-butylphenol and elemental sulfur (54% yield).[15] The ready availability of **3** in substantial quantities has allowed us to investigate and develop its functions.[16] As a remarkable result of the replacement of X=CH_2 by S, **3** can extract transition metal ions such as Co^{2+}, Cu^{2+} and Zn^{2+} quantitatively from aqueous phase



	X	R
1	CH_2	Bu^t
2	CH_2	Oct^t
3	S	Bu^t
4	S	Oct^t
5	SO	Bu^t
6	SO	Oct^t
7	SO_2	Bu^t
8	SO_2	Oct^t

Scheme 1. Structures of calix[4]arenes. Oct^t denotes 1,1,3,3-tetramethylbutyl group.

☆ See Ref. 1.

Keywords: calixarenes; complexation; sulfides; oxidation.

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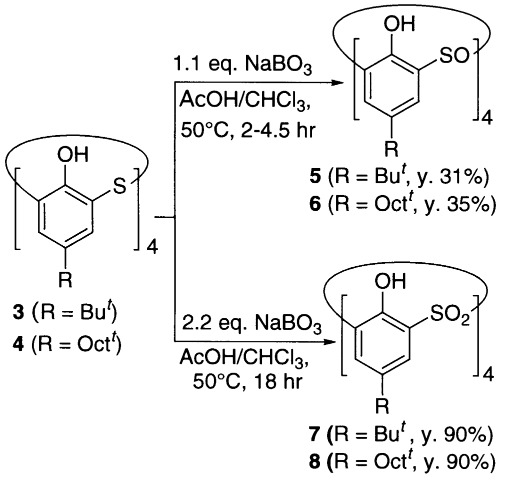
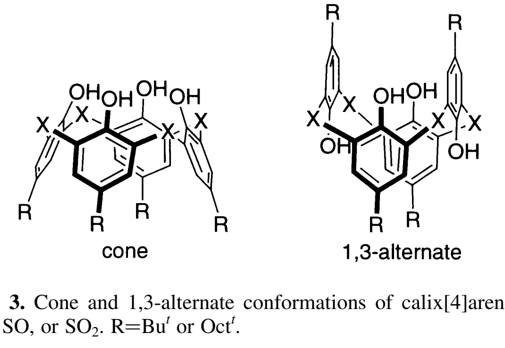


Scheme 2. Oxidation of bridging sulfur in thiacalix[4]arenes.

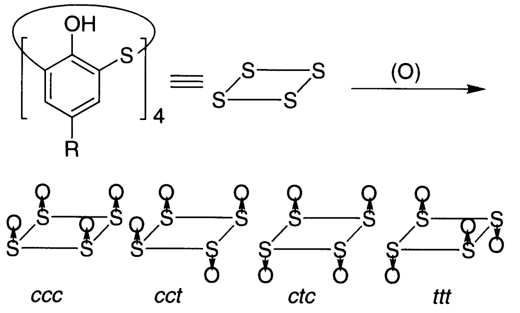
into organic phase. On the other hand, **1** could not extract them at all under the same conditions, clearly indicating the important role of the bridging entity X in the metal extraction.[17]

Soon after the synthesis of thiacalix[4]arenes **3** and **4**, we realized that the bridging epithio function would provide the base for various transformations which could not be attained by the conventional methylene-bridged calixarenes. In this context, we reported in a previous communication[1] that controlled oxidation of thiacalix[4]arene (**3**,**4**) affords practical routes to the synthesis of sulfinyl-(**5**,**6**) and sulfonylcalix[4]arenes (**7**,**8**). Also reported were the intrinsic metal ion selectivities of these sulfur containing calix[4]arene analogs, reconfirming the importance of the bridging entities as evidenced by solvent extraction studies; **3** preferred transition metal ions, while **8** liked alkaline earth metal ions, and quite interestingly, **5** could bind to both transition and alkaline earth metals. These make sharp contrast to the common understanding that methylene-bridged **1** could not bind to any of them in solvent extraction systems.

Needless to say, the binding property of host molecules to various kinds of metal ions is an indispensable information to design molecular receptors and functional devices. The aims of this paper are firstly to describe the details of the syntheses of sulfinyl-(**5**,**6**) and sulfonyl-(**7**,**8**) analogs of thiacalix[4]arenes (**3**,**4**), and secondly to report the results of a comprehensive study on the binding ability of calix[4]arenes **2**, **4**, **6**, and **8** to a quite wide range of metal ions commonly available to elucidate the role of the bridging groups X (=CH_2, S, SO, and SO_2).



Scheme 3. Cone and 1,3-alternate conformations of calix[4]arenes. X=CH_2, S, SO, or SO_2. R=Bu^t or Oct^t.



Scheme 4. Four possible stereoisomers of sulfinylcalix[4]arene by combination of configuration of four S=O groups. Abbreviations *ccc*, *cct*, *ctc*, and *ttt* stand for *cis–cis–cis*, *cis–cis–trans*, *cis–trans–cis*, and *trans–trans–trans*, respectively. Conformational isomers by orientation of phenyl groups are omitted for clarity.

2. Results and discussion

2.1. Syntheses of sulfinyl- and sulfonylcalix[4]arenes

As was reported briefly in the previous communication,[1] all four epithio groups of thiacalix[4]arene **3** were readily oxidized to give the sulfinyl or sulfonyl counterparts (Scheme 2). Thus, heating a mixture of thiacalix[4]arene **3** and a 2.2-fold excess of $NaBO_3$ as oxidizing agent in CH_3COOH–$CHCl_3$ gave the corresponding sulfonyl analog **7** in an excellent yield. Hydrogen peroxide could also be used as the oxidant (see Section 4).[18] On the other hand, reduction of the amount of $NaBO_3$ to a 1.1 M equivalent enabled the isolation of sulfinylcalix[4]arene **5** in moderate but acceptable yield, the reaction mixture of which seemingly contained calixarenes with variously oxidized sulfur bridges that were eventually end in the sulfonyl derivative **7**.

It has been shown by X-ray crystallography that **1** and **3** adopt cone conformation in the solid state,[19,15b] while **5** and **7** have 1,3-altenate conformation (Scheme 3).[18,20] It should be noted that sulfinylcalix[4]arene (e.g. **5**) has theoretically four possible stereoisomers depending on the disposition of the four SO groups, even if the flip-flop motion of the phenol units is taken into account (Scheme 4). The oxidation of thiacalix[4]arene **3**, however, allowed the isolation of **5**, in which the four SO groups are arranged in a *trans–trans–trans* (all-*trans*) configuration in regard to any of the two adjacent SO pairs. The preferential formation of this particular stereoisomer among the four may, at least partly, be ascribed to the least electronic repulsion brought about by the highly dipolar SO groups.[21]

From the view point of solubility in organic solvent (vide infra), it seemed that *tert*-octyl group[22] is preferable to *tert*-butyl as the *p*-substituent. Therefore, *p*-*tert*-octylthiacalix[4]arene **4**[15b] was subjected to the same oxidation protocol to afford the corresponding sulfinyl and sulfonyl counterparts **6** and **8** in similar yields (Scheme 2). These *p*-*tert*-octylcalixarenes (**4**, **6**, and **8**) gave similar NMR data to those of the *tert*-butyl counterparts (**3**, **5**, and **7**) except

Table 1. The $E\%$ values of metal ions by **2**, **4**, **6**, and **8**

(a) Soft to intermediate metal ions

M	Mn^{2+}	Fe^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Pd^{2+}	Ag^{+}	Cd^{2+}	Au^{3+}	Hg^{2+}	Pb^{2+}	Bi^{3+}
pH	8.0	6.8	8.0	8.0	8.0	8.0	–[a]	5.9	8.4	–[b]	7.9	6.3	2.8
2	6	12	2	0	6	6	14	6	–[c]	21	0	3	–[c]
4	80	37	98	99	91	100	73	99	98	31	100	89	42
6	56	100	99	64	10[d]	79	92	–[c]	14[d]	38	0	89[e]	78[e]
8	72[f]	90[f]	9	2	4	10	15	–[c]	4	12	0	0[e]	26[e]

(b) Hard metal ions

M	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Y^{3+}	Pr^{3+}	Eu^{3+}	Ti^{4+}	Zr^{4+}	Hf^{4+}
pH	9.8	9.8	9.8	9.8	6.0	6.3	6.3	2.2	1.4	1.4
2	0	6	0	0	9	0	0	3	21	0
4	0	2	0	0	5	3	0	4	22	0
6	55	69	10[d]	9[d]	98	100	100	99	100	100
8	56	100	95	80	44	100	100	75	99	99

(c) Those extracted only by **6**

M	Be^{2+}	Sc^{3+}	V^{5+}	Nb^{5+}	Ta^{5+}	Ru^{3+}	Al^{3+}	Ga^{3+}	In^{3+}
pH	5.3	2.8	2.8	4.8	4.8	3.3	3.5	3.0	4.9
2	0	8	0	8	5	3	3	9	–[c]
4	0	2	2	13	5	5	8	0	0
6	100	100	41	85	1	68	100	97	42
8	0	10	5	12	2	0	7	0	5

(d) Those not extracted by **2**, **4**, **6**, and **8**

M	Li^{+}	Na^{+}	K^{+}	Rb^{+}	Cs^{+}	Cr^{3+}	Mo^{6+}	Rh^{3+}	Pt^{2+}	Tl^{+}	Sb^{3+}
pH	9.7	9.7	9.7	9.7	9.7	5.1	5.0	5.9	9.9	5.7	9.7
2	0	2	0	0	7	9	0	6	9	0	0
4	0	1	0	1	7	3	0	2	1	3	3
6	17	23	0	1	12	8	0	9	3	2	0
8	18	4	0	0	14	8	0	5	4	2	0

$E\% = 0$ means less than 0.4%.

[a] In 0.05 M HNO_3 solution.

[b] In 1.0 M HNO_3 solution.

[c] The $[Metal]_{aq}$ was not measured due to the formation of precipitate of the unknown species.

[d] These metal ions were extracted by use of 2×10^{-3} M **6**; Cu^{2+} 81% at pH 4.8, Cd^{2+} 44% at pH 8.3, Sr^{2+} 90% at pH 10.6, Ba^{2+} 85% at pH 10.6.

[e] Me_4NNO_3 instead of Me_4NCl was added in aqueous phase.

[f] The metal ion M^{2+} may be oxidized to M^{3+} by complexation with **8** to give high $E\%$.

that **6** gave splitted ^{1}H NMR patterns for methyl protons at 1 and methylene protons at 2 position of *tert*-octyl group (see Section 4), providing another evidence of the all-*trans* configuration of the four S=O groups. Thus, we have now sufficient amounts of S-, SO-, and SO_2-bridged *p*-*tert*-octylcalixarenes in hand to carry out solvent-extraction study to elucidate the role of the bridging moiety X.

2.2. Coordination abilities toward metal ions

The metal-binding ability of calix[4]arene ($X=CH_2$) and the analogs with X=S, SO, and SO_2 was assessed by solvent extraction toward almost all available metal ions except radioactive ones. It was found that calix[4]arenes **2**, **4**, **6**, and **8** provided a higher solubility to the formed metal complexes in chloroform than *tert*-butyl counterparts did.[1] The pH of the aqueous phase was varied in the range where metal hydroxides did not form. The percent extraction, $E\%$, for various metal ions by **2**, **4**, **6**, and **8** were calculated by Eq. (1)

$$E\% = ([\text{metal}]_{\text{aq,init}} - [\text{metal}]_{\text{aq}})/[\text{metal}]_{\text{aq,init}} \times 100\% \qquad (1)$$

where $[\text{metal}]_{\text{aq,init}}$ and $[\text{metal}]_{\text{aq}}$ are the concentrations of metal ions in aqueous phase before and after extraction, respectively.

Table 1 lists the $E\%$ values of metal ions at representative pH, which was mainly categorized by hardness and softness of the ions.[23] Soft metal ions such as Ag^{+} and Hg^{2+} were extracted only by **4**, whereas many of the first transition metal ions were extracted by **4** and **6** (Table 1a). On the other hand, hard metal ions were extracted by **6** and **8** (Table 1b). It is interesting that Be^{2+}, Ru^{3+}, Al^{3+}, Ga^{3+}, In^{3+}, Sc^{3+}, V^{5+} and Nb^{5+} were extracted only by **6** (Table 1c). Note that metal ions such as alkali metal ions, Cr^{3+}, Mo^{6+}, Rh^{3+}, Sb^{3+}, Ta^{5+}, Pt^{2+} and Tl^{+} could not be extracted under the conditions examined (Table 1d).

The above-mentioned results were summarized as follows in periodic tables (Fig. 1) by defining the metals of $E\%$ greater than 30% as extracted. The methylene bridged **2** could not extract any of the metal ions examined (Fig. 1a). Roughly speaking, **4** extracted soft to intermediate metal ions (Ag^{+}, Hg^{2+}, and first transition metal ions) very well, but showed little affinity to hard metal ions

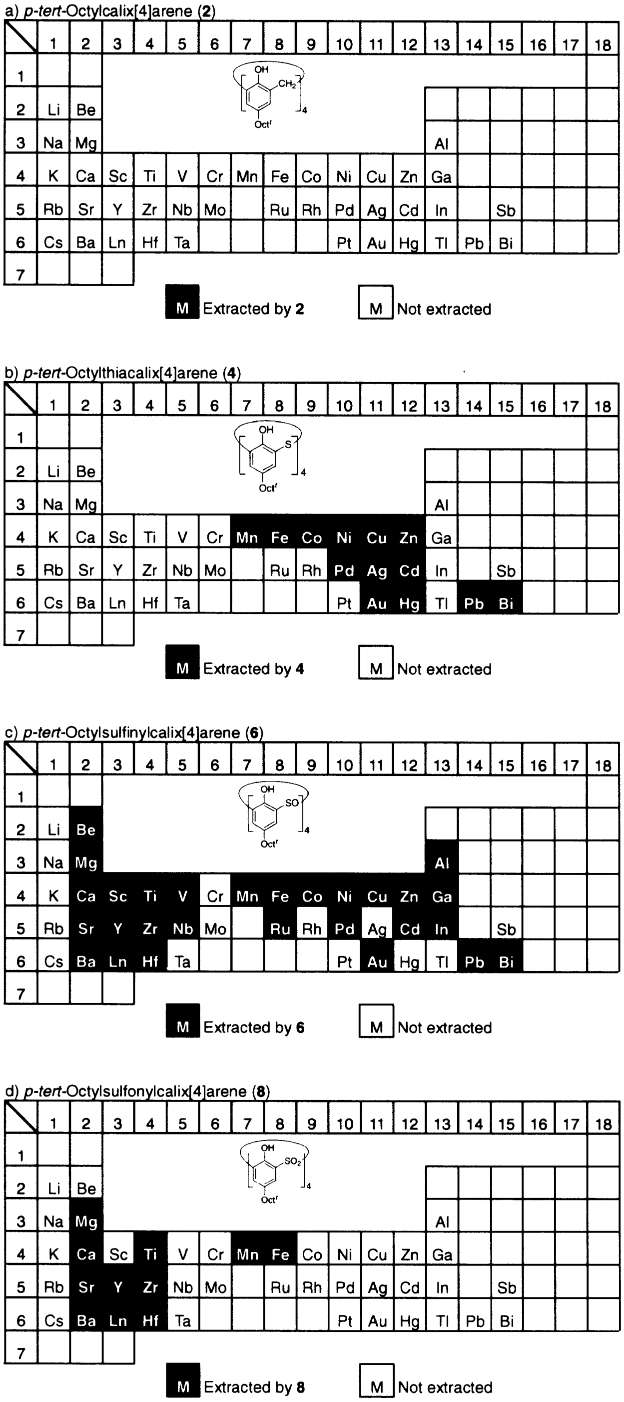


Figure 1. Periodic tables of the extracted metal ions ($E\% > 30\%$) by *p-tert*-octylcalix[4]arene **2**, and the analogs with S (**4**), SO (**6**), and SO_2 (**8**) bridges in place of CH_2.

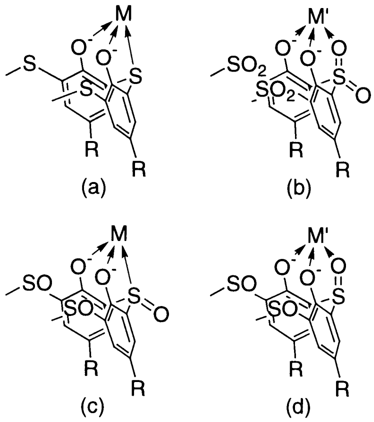


Figure 2. Proposed coordination manners of *p-tert*-octylthiacalix[4]arene (**4**) and the sulfinyl (**6**) and sulfonyl (**8**) analogs. R=Oct′. For clarity, only half part of calix[4]arene ring is depicted. *M* and *M*′ denote soft and hard metal ions, respectively.

(Fig. 1b). On the other hand, the sulfone **8** far preferred harder metal ions (alkaline earth metal ions, lanthanoid ions, Ti^{4+}, Zr^{4+} and Hf^{4+}, see Fig. 1d). Interestingly, the sulfoxide counterpart **6** could extract many of not only soft but also hard metal ions (Fig. 1c).

Previously, we reported a detailed study of extraction of Zn^{2+} ion with **3**, showing that the extracted 1:1 complex contained the metal center ligated by one of the four bridging sulfurs in addition to the adjacent two phenoxide oxygens to form two sets of five-membered chelated rings as evidenced by ^{1}H NMR study.[17] Although the 1:1 complex was converted to a 3:4 (=**3**/Zn) complex by losing some ligand on recrystallization from benzene–methanol, the above coordination mode by O^-, S, O^- was unambiguously substantiated by X-ray crystallography of the 3:4 complex.[24]

Considering the tridentate ability of **3** to Zn^{2+} ion, herein we would like to propose the coordination modes depicted in Fig. 2 to explain the results of metal extraction by **4**, **6**, and **8**.[1] First, **4** may bind to soft metal ions by the coordination of a lone pair electrons of sulfur atom besides two phenolic oxygens (Fig. 2a) as proven for the Zn^{2+} complex with **3**.[24] Second, lacking the lone pair electrons on S, **8** could not coordinate to soft metal ions but did to hard metal ions by ligation of sulfonyl oxygen (Fig. 2b).[25] Third, **6** could switch the coordinating atom between S and O of sulfinyl group depending on the hardness and softness of the metal ions (Fig. 2c and d).[26] In other words, the extraction selectivity of these sulfur bridged calix[4]arenes (**4**, **6**, and **8**) may be explained by the 'hard and soft acids and bases (HSAB) rule'.[23] Here, it is assumed that the adjacent phenol moieties of **6** and **8** orient to the same direction (i.e. *syn* manner) to facilitate the coordination of two phenolate oxygens to metal ions (Fig. 2b–d),[27] although the corresponding *tert*-butyl counterparts **5** and **7** adopt 1,3-alternate conformation in the solid state as stated above (i.e. *anti* manner for adjacent phenyl groups). The fact that several hard metal ions (such as Be^{2+}) could be extracted only by **6** but not by **8** may suggest that the electron density on oxygen atom of sulfinyl group is higher than the one of sulfonyl group to coordinate to the cationic center.

Consideration of the results of the solvent extraction study may provide some cues to possible applications. For example, hard and soft metal ions could be separated each other by extraction by using **4** or **8**. Furthermore, although Nb^{5+} and Ta^{5+} ions are much alike in chemical properties, the sharp difference in the extractability between them by **6** (Table 1c) may be reliable for separating them. Another finding of interest is the strong coloration of organic phase upon extraction of some metal ions by **6**; Fe^{2+} gave light red whereas V^{5+} and Ru^{3+} gave purple color, meaning that **6** is a potential candidate for chromogenic receptor for those metal ions.

3. Conclusion

It has been demonstrated that the oxidation of sulfide linkages of thiacalix[4]arenes to sulfoxides and sulfons were readily accomplished by controlling the stoichiometry of oxidizing agent. The solvent extraction study of thiacalix[4]arene and the sulfinyl and sulfonyl analogs toward quite a wide variety of metal ions showed that selectivity toward metal ions greatly depended upon the oxidation state of the sulfur moiety, which is best understood by HSAB rule assuming a crucial role of the coordination of the bridging groups to metal ions. This hypothesis of the metal selectivity of thia-, sulfinyl- and sulfonylcalix[4]arenes may be highly useful for investigating the structures, physicochemical properties, and functions of the metal complexes.

4. Experimental

4.1. General methods

Mps were taken using a Yamato MP-21 apparatus and are uncorrected. Microanalyses were carried out in the Institute of Chemical Reaction Science, Tohoku University. Merck silica gel 60GF254 was used for TLC. ^{1}H NMR was measured on a Bruker DPX-400 spectrometer operated at 400 MHz. IR spectra were obtained with a Shimadzu IR-460. Mass spectra were recorded with a JEOL JMS-GC mate GC–MS system.

4.2. Materials

Unless stated otherwise, reagent-grade reagents and solvents were used as received from chemical suppliers. The calixarenes **1**,[28] **2**,[4a] **3**,[15] and **4**[15] are synthesized as described in the literatures. Standard solutions for metal ions were purchased from Kanto Kagaku, Tokyo. The pH buffers tris(hydroxymethyl)aminomethane (Tris), 2-morphorinoethanesulfonic acid (MES), piperazine-1,4-bis(2-ethanesulfonic acid) (PIPES), and *N*-cyclohexyl-2-aminoethanesulfonic acid (CHES) were purchased from Wako Pure Chemical Industries, Osaka.

4.2.1. *p-tert*-Butylsulfinylcalix[4]arene (5). In a typical run, to a solution of **3** (2.0 g, 2.76 mmol) in chloroform (40 cm^3) were added acetic acid (50 cm^3) and $NaBO_3 \cdot 4H_2O$ (1.9 g, 12 mmol). After the mixture had been stirred at 50°C for 4.5 h, **5** was extracted with chloroform (30 cm^3×3). After phase separation, methanol was added to the chloroform phase to precipitate the product, which was recrystallized from dichloromethane–methanol and dried in vacuo (80°C, 12 h) to give a pure sample of **5** (0.67 g, 30.7%). Mp 295°C (decomp.). FAB MS *m/z* 785 ($M^+ +1$). IR (KBr) 3188 (OH), 2953(CH), 1001 (SO) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ=1.29 (36H, s, $C(CH_3)_3$), 7.65 (8H, s, Ar–H), 9.30 (4H, s, OH). ^{13}C NMR (400 MHz, $CDCl_2CDCl_2$, TMS) δ=31.1 ($C(CH_3)_3$), 34.5 ($C(CH_3)_3$), 122.5 and 127.7 (C_{Ar}–SO), 123.9 and 130.0 (C_{Ar}–H), 142.1 (C_{Ar}–Bu^t), and 152.4 (C_{Ar}–OH), which were unambiguously assigned by DEPT. Found: C, 60.88; H, 6.12; S, 16.06%. Calcd for $C_{40}H_{48}O_8S_4$: C, 61.19; H, 6.16; S, 16.34%.

4.2.2. *p-tert*-Octylsulfinylcalix[4]arene (6). To a solution of **4** (3.0 g, 3.18 mmol) in chloroform (60 cm^3) were added acetic acid (75 cm^3) and $NaBO_3 \cdot 4H_2O$ (2.1 g, 14 mmol). After the mixture had been stirred at 50°C for 2 h, **6** was extracted with chloroform (30 cm^3×3). After phase separation, methanol was added to the chloroform phase to precipitate the product, which was recrystallized from dichloromethane–methanol and dried in vacuo (80°C, 12 h) to give a pure sample of **6** (1.11 g, 34.6%). Mp 280–282°C (decomp.). FAB MS *m/z* 1009 ($M^+ +1$). IR (KBr) 3294 (OH), 2951(CH), 1015 (SO) cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ=0.74 (36H, s, $-C(CH_3)_2CH_2C(CH_3)_3$), 1.27 and 1.36 (12H, s, $-C(CH_3)_2CH_2C(CH_3)_3$), 1.63 and 1.69 (4H, d, J_{gem}=−14.8 Hz, $-C(CH_3)_2CH_2C(CH_3)_3$), 7.60 (8H, s, Ar–*H*), 9.25 (4H, s, –O*H*). ^{13}C NMR (400 MHz, $CDCl_2CDCl_2$, TMS) δ=29.5, 31.8, 32.4, 38.6, 40.6, 57.3 ($-C(CH_3)_2CH_2C(CH_3)_3$), 142.2 (C_{Ar}–Oct^t), and 152.6 (C_{Ar}–OH). The ^{13}C resonances for *ipso* carbons with respect to H and S=O group were not observed possibly due to the long spin-lattice relaxation time caused by the introduction of bulky *tert*-octyl group. Found: C, 66.57; H, 7.91; S, 12.75%. Calcd for $C_{56}H_{80}O_8S_4$: C, 66.62; H, 7.99; S, 12.71%.

4.2.3. *p-tert*-Butylsulfonylcalix[4]arene (7). In a typical run, to a solution of **3** (1.0 g, 1.38 mmol) in chloroform (30 cm^3) were added acetic acid (50 cm^3) and $NaBO_3 \cdot 4H_2O$ (2.0 g, 13 mmol). After the mixture had been stirred at 50°C for 18 h, **7** was extracted with chloroform (30 cm^3×3) and worked up as usual. The product was recrystallized from benzene–methanol and dried in vacuo (80°C, 12 h) to give a pure sample of **7** (1.06 g, 90.0%). Mp>360°C; FAB MS *m/z* 849 ($M^+ +1$); IR (KBr) 3354 (OH), 2964 (CH), 1319, 1159 (SO_2) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29 (36H, s, $C(CH_3)_3$), 8.13 (8H, s, Ar–H), OH protons (4H) were not detected. ^{13}C NMR ($CDCl_2CDCl_2$) δ 30.8 ($C(CH_3)_3$), 34.6 ($C(CH_3)_3$) and 125.9 and 133.2 (C_{Ar}). Two of the $^{13}C_{Ar}$ resonances were not observed possibly due to their long relaxation time. Calcd for $C_{40}H_{48}O_{12}S_4$: C, 56.58; H, 5.70; S, 15.11. Found: C, 56.63; H, 5.68; S, 15.01.

4.2.4. *p-tert*-Octylsulfonylcalix[4]arene (8). For instance, **4** (100 mg, 0.07 mmol) was dissolved in chloroform (2 cm^3) and then acetic acid (3 cm^3) and $NaBO_3 \cdot 4H_2O$ (0.14 g 0.93 mmol) were added. The mixture was stirred at 50°C for 18 h. After being cooled, the reaction mixture was added 2 M HCl (2 cm^3) product was extracted with chloroform (3 cm^3×3) and washed with 6 M HCl aq. soln. (2 cm^3×3). The chloroform solution was evaporated to dryness to give crude product, which was then recrystallized from benzene–methanol mixture to give a pure sample of **8** (102 mg, 90.1%). Procedure using hydrogen peroxide as an oxidizing agent; **4** (2.0 g, 1.38 mmol) was dissolved in chloroform (40 cm^3) and then trifluoroacetic acid (10 cm^3) and an aq. soln. of hydrogen peroxide (30%, 20 cm^3) were added. The mixture was stirred at 80°C for 24 h. After being cooled, the reaction product was extracted with chloroform (30 cm^3×3) and worked up as the same above to give essentially pure sample of **8** (1.80 g, 79.5%). Compound **8**: mp 336°C (decomp.); FAB MS *m/z* 1074 ($M^+ + 1$); IR (KBr) 3389 (OH), 2957 (CH), 1306, 1140 (SO_2) cm^{-1}; ^1H NMR ($CDCl_3$) $\delta = 0.68$ (36H, s, $-C(CH_3)_2CH_2C(CH_3)_3$), 1.32 (24H, s, $-C(CH_3)_2CH_2C(CH_3)_3$), 1.73 (8H, s, $-C(CH_3)_2CH_2C(CH_3)_3$), 8.10 (8H, s, Ar–H); OH protons (4H) were not detected. ^{13}C NMR ($CDCl_3$) δ 31.1, 31.8, 32.3, 38.7, 56.5, ($-C(CH_3)_2CH_2C(CH_3)_3$) and 126.9, 133.7, 143.9, and 151.2 (C_{Ar}). Calcd for $C_{56}H_{80}O_{12}S_4$: C, 62.65; H, 7.51; S, 11.95. Found: C, 62.53; H, 7.34; S, 11.76.

4.3. Solvent extraction

The procedure for solvent extraction is as follows. To a vial tube were pipetted an aqueous solution (10 cm^3) containing metal ion ($[Metal]_{aq,int} = 1.0 \times 10^{-4}$ M), Me_4NCl (0.1 M) for **6** and **8** as well as a pH buffer (0.05 M) and a 10 cm^3 of chloroform solution ([**2**, **4**, **6** or **8**$=5.0 \times 10^{-4}$ M). The mixture was shaken for 24 h at 300 strokes per min at 23±2°C. After the aqueous phase was separated by centrifugation, the total concentration of the metal species remaining in the aqueous phase, $[Metal]_{aq}$, was measured by atomic absorption spectrometer or inductively coupled plasma atomic emission spectrophotometer. The pH of the aqueous phase was adjusted with HNO_3–NH_3 (1.0–2.2), glycine–HNO_3 (2.5–3.5), succinic acid–NH_3 (4.0–5.0), MES–NH_3 (5.5–6.0), PIPES–NH_3 (6.3–7.0), Tris-HNO_3 or Tris-HCl (7.5–8.5), CHES–NH_3 or NH_3–HCl (9.0–10.0). The formation of ion pairs of **6** and **8** with Me_4N^+ prevented them from precipitating at the interface between two phases. In this study, the metal species V^{5+}, Mo^{6+}, Zr^{4+}, and Hf^{4+} denote VO_2^+, MoO_2^{2+}, ZrO^{2+}, and HfO^{2+}, respectively. Nb^{5+} and Ta^{5+} were used as the solutions in 1.0 M HF.

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