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First Synthesis and Properties of Calix[4]arene with Two Alternately Arranged Phloroglucinols and Two *p-tert*-Butylphenols

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The Calix[4]arene 1 including two alternately arranged phloroglucinols and *p-tert*-butylphenols was synthesized via the "3 + 1" coupling procedure, and its p*Ka* values were estimated to be 3–4 and 7.5, while those of the other six phenolic hydroxyls were approximately 11. Its UV–vis spectrum at pH 11 and ^{1}H and ^{13}C NMR spectra in NaOD-D_2O solution (pH 12.8) showed a dramatic change like those of the phloroglucinol when compared to those in acidic or neutral solution, which suggests a change in the phloroglucinol moiety to the keto-form. During the solvent extraction for alkali metal species using 1, Li^+ was only extracted in the low yield of 15% at pH 11. The cyclic voltammetry study of 1 was used to compare it with the phloroglucinol and *p-tert*-butylphenol. The redox potential of the corresponding two phloroglucinols was observed in 1.

Keywords: Calix[4]arene; Phloroglucinol; Keto-tautomer; p*Ka*; Solvent extraction; Redox potential

INTRODUCTION

Many calix[n]arene derivatives have been synthesized because of their easy synthesis and the easy introduction of functional groups into them [1]. However, the already synthesized polyphenol-class of calix[n]arenes has been limited to the phenol, resorcinol, or hydroxyhydroquinone derivatives, as far as we know. Among the polyphenols, it is well known that phloroglucinol (1,3,5-benzenetriol) is readily changed into keto-tautomers in alkaline solution. If the calix[n]arene including the phloroglucinols is synthesized, it is expected that its phloroglucinol moiety will change into the keto-tautomer under alkaline conditions, then show different properties and behaviors than under acidic or neutral conditions (Fig. 1).

On the basis of this hypothesis, we planned the first synthesis of the simplest calix[4]arene alternately linked with two *p-tert*-butylphenols and two phloroglucinols (Scheme 1). Based on this synthetic strategy, the trimer **4** is first synthesized by the condensation reaction of 1 equivalent of 4-*tert*-butyl-2,6-dihydroxymethylphenol (**3**) and 2 equivalents of 1,3,5-trimethoxybenzene (**2**). Next, the cyclic tetramer **5** is synthesized via a "3 + 1" approach by the condensation reaction of the trimer **4** with **3** under highly dilute concentration conditions in the presence of a catalytic amount of *p*-toluenesulfonic acid (*p*-TsOH) [2–4]. Finally, the demethylation with boron tribromide (BBr_3) affords the desired calix[4]-arene **1**. Its structure analysis was carried out using FAB-MS and ^{1}H and ^{13}C NMR spectroscopies. Furthermore, its properties and behavior in solution were explored regarding the p*Ka*, redox potential, and solvent extraction for alkali metal species.

RESULTS AND DISCUSSION

The synthesis of **1** was carried out based on our described synthetic strategy. The trimer **4** was synthesized with a yield of 57% by stirring for 6 h at 60°C in the presence of 0.2 equivalents of *p*-TsOH by the dropwise addition of a toluene solution of **3** (1 equiv.) prepared in the usual way [5,6] to a toluene solution of **2** (4 equiv.). The calix[4]arene **1** was synthesized by the condensation of equimolar

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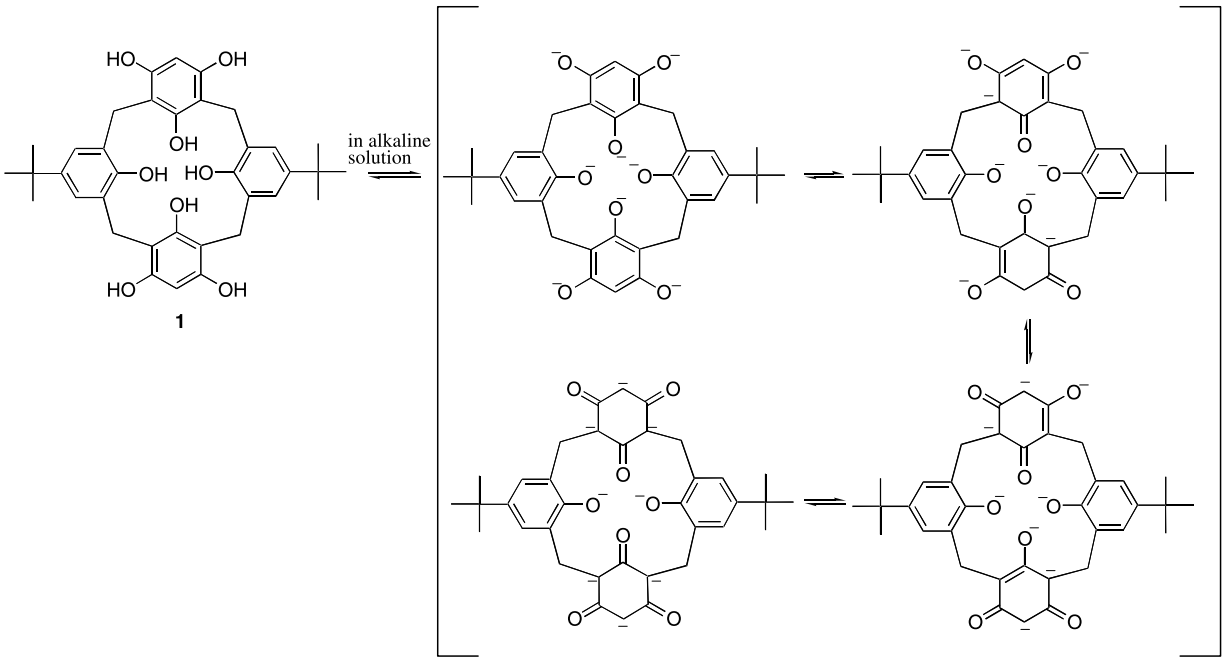
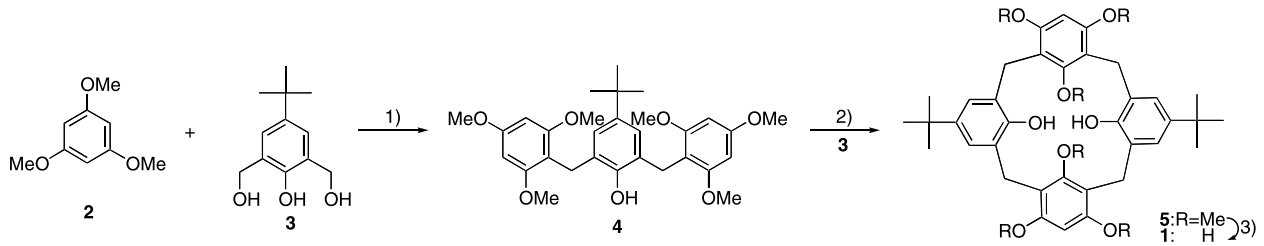


FIGURE 1 Presumed calix[4]arene's tautomerism in alkaline solution.

amounts of trimer **4** and **3** in the presence of 0.15 equivalents of *p*-TsOH under highly dilute concentration (5.9×10^{-4} M) conditions. Subsequent demethylation of **5** using 30 equivalents of BBr_3 was performed with a good yield of 90%. The calix[4]arene **1** was finally recrystallized from chloroform ($CHCl_3$) and synthesized in an overall yield of 19% from **3**, and its solubility was as follows: soluble in ethyl acetate (AcOEt), methanol (MeOH), DMSO, and alkaline aqueous solution, while sparingly soluble in chloroform, and insoluble in water.

The ^{1}H and ^{13}C NMR spectra of **1** in DMSO-d_6 (Figs 2c and 4a) suggest that the structure of **1** is symmetrical. In the ^{1}H NMR spectrum of **1** in DMSO-d_6, two singlet peaks for four phenolic protons were observed at 9.20 and 9.88 ppm, which suggests that both the phenolic hydroxyls of the *tert*-butylphenol and phloroglucinol moieties are strongly hydrogen-bonded [7–12], and the remaining outside four phenolic hydroxyls of the two phloroglucinol moieties are also present under equivalent conditions. When one drop of D_2O was added to the DMSO-d_6 solution of **1**, the area of the broader singlet peak at 9.88 ppm decreased. Next, **1** was dissolved in D_2O by the addition of 30 µl of a 40% NaOD-D_2O solution, and the pH of this aqueous solution was 12.8. This solution was subjected to the measurement of the ^{1}H and ^{13}C NMR spectra (Figs 2d and 4b) and compared to those measured in DMSO-d_6. In its ^{1}H NMR spectrum (Fig. 2d), an aromatic proton of the phloroglucinol moiety at 5.94 ppm disappeared and two pairs of doublet peaks derived from four methylene groups were split and more clearly observed; the chemical shift between a pair of doublet peaks was greater than those in DMSO-d_6. Thus, it means the conversion of four pairs of equivalent methylene-protons into two pairs of equivalent methylene-protons, in which each of the two protons of the methylene moiety is not equivalent. This change in the methylene peak shows the change in the ring-structure of **1** in alkaline solution. In its ^{13}C NMR spectrum (Fig. 4b), new three peaks were observed at 194.5, 187.9, and 185.5 ppm compared to those in DMSO-d_6 (Fig. 4a),



Reagents and conditions 1) p-TsOH in toluene, 60ºC 5h Y:57% 2) *p*-TsOH in toluene (*c* 5.9 x10^{-4} mmol/l), reflux 8h, Y:37%
3) BBr_3 in CH_2Cl_2, –78ºC~ r.t. 24h, Y:90%

SCHEME 1 Synthesis of calix[4]arene with two alternately arranged two phloroglucinols.

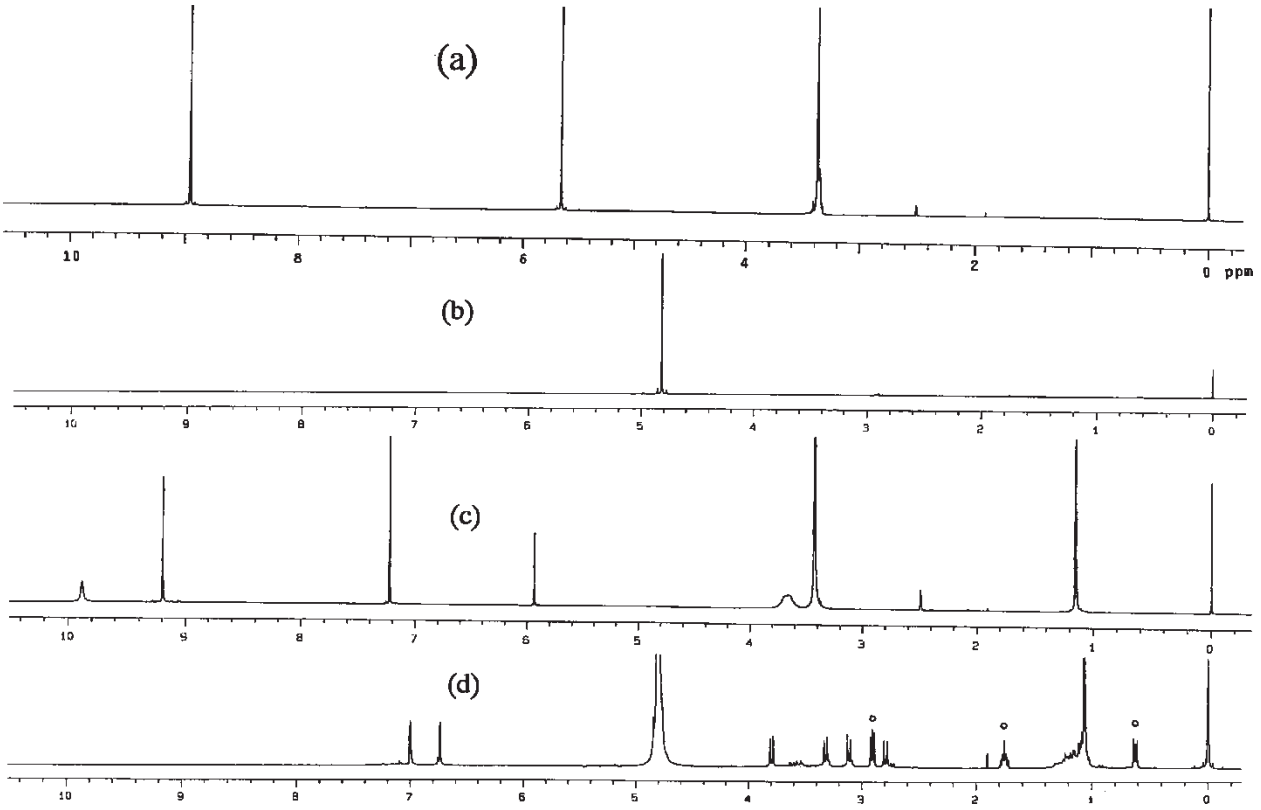


FIGURE 2 ^{1}H NMR spectra of phloroglucinol and **1**, (a) phloroglucinol in DMSO-d_6, (b) phloroglucinol in NaOD-D_2O solution (pH 13.3), (c) **1** in DMSO-d_6, and (d) **1** in NaOD-D_2O solution (pH 12.8). °; peaks of 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt used as the internal standard.

which may be peaks derived from the carbonyl carbons formed by the keto-form. These changes were similarly observed in ^{1}H and ^{13}C NMR spectra of phloroglucinol in NaOD-D_2O solution; thus, its ^{1}H NMR spectrum (Fig. 2b) has no peaks, and its ^{13}C NMR spectra in pH 8.9, 9.3, and 13.3 (Figs 3a–c) show that four peaks were gradually observed at 46, 100, 188, and 198 ppm in the place of two peaks at 98 and 162 ppm, with the rise of the solution pH. The ^{13}C NMR spectrum of **1** in NaOD-D_2O solution (pH 12.8, Fig. 4) also observed the same change as that of phloroglucinol. These results suggest the change of phloroglucinol into the keto-form in alkaline solution. Since two peaks derived from the methylene carbon were observed at 26.4 and 31.2 ppm and the peaks derived from the aromatic carbons were also observed to be more complicated than those in DMSO-d_6, it is suggested that the ring-structure of **1** changed from symmetrical to unsymmetrical. Thus, based on the above NMR analysis, it is suggested that six phenolic hydroxyls including the two *tert*-butylphenols dissociated all at around pH 12, and the two phloroglucinol moieties changed into the keto-tautomers and simultaneously the calix-ring may have changed into the unsymmetrical structure, and **1** may be present in a state of complicated equilibrium as shown in Fig. 1. Many small peaks were observed in the ^{1}H and ^{13}C NMR spectra of **1** in alkaline solution. Most of this is due to the presence of many complicated equilibriums of **1**, and **1** is also not very stable in alkaline solution. (After the NMR measurement, the alkaline solution of **1** was poured into a HCl aqueous solution and **1** was extracted with AcOEt. On the TLC (1:1 *n*-hexane-AcOEt) of the recovered **1**, small amounts of impurities were observed around the original point.)

The p*K*a-value of **1** was estimated from the potentiometric titration and photometric pH titration [7–16]. The p*K*a value was first determined to be 3–4 and 7.5 from the consumption of a KOH solution equivalent to a proton during a potentiometric titration (Fig. 5). Furthermore, the other p*K*a values were estimated by photometric pH titration (Figs 6–8). A significant change in the UV–vis spectrum of **1** at around pH 11–12 (two new absorption peaks appeared at 256.5 and 369.5 nm analogous to that of phloroglucinol) allowed us to expect that the hydrogen bond linking the four phenolic hydroxyls on the lower rim of the corn-type calix[4]arene was broken and the structure of the two phloroglucinol moieties significantly changed to the keto-tautomers, while the UV–vis spectrum of the phloroglucinol significantly changed at pH 9.2 [17,18] (Fig. 6). Thus, the p*K*a-values of the six phenolic hydroxyls including two *tert*-butylphenolic hydroxyls were all approximately 11 [7], which were estimated from the

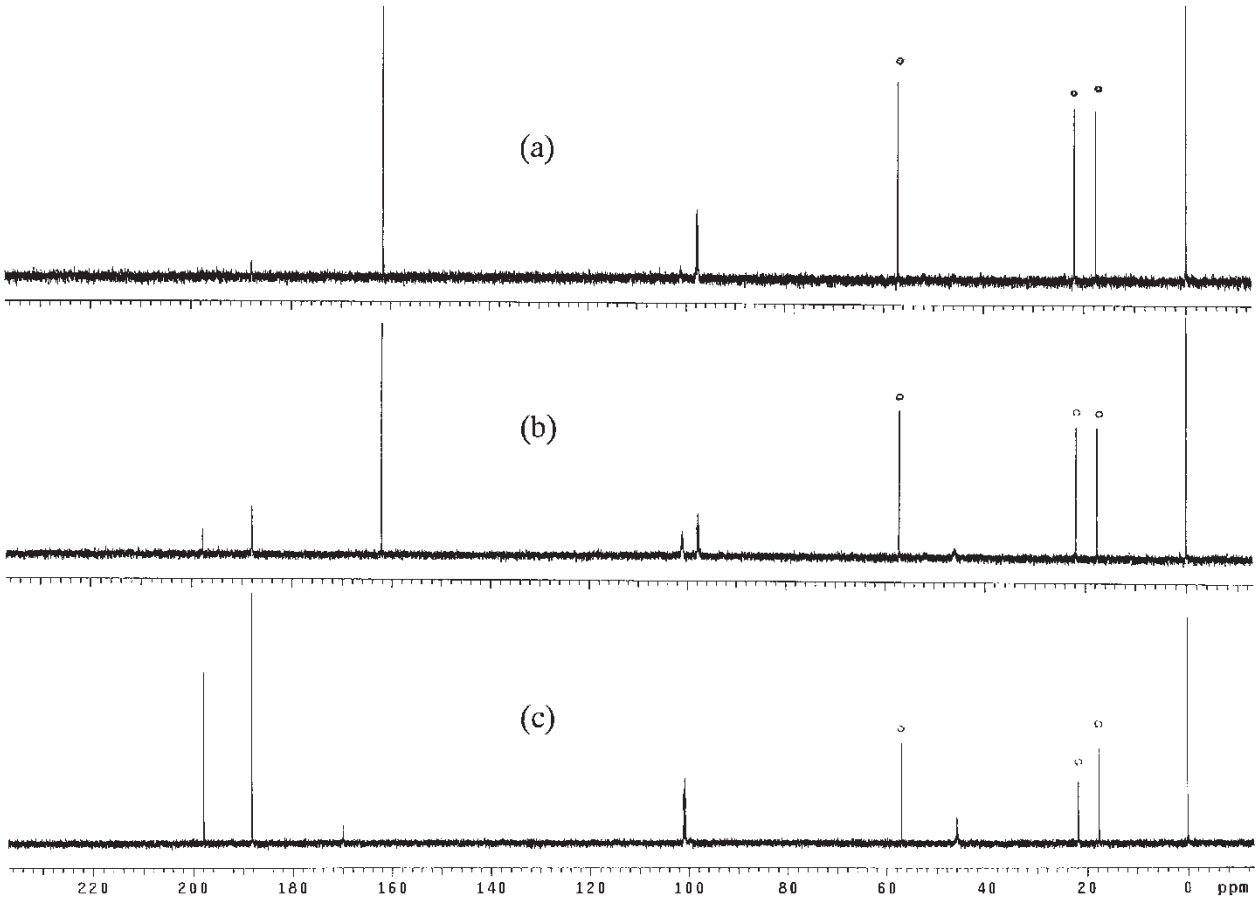


FIGURE 3 ^{13}C NMR spectra of phloroglucinol in NaOD-D_2O solution, (a) pH 8.9, (b) pH 9.3, and (c) pH 13.3.

changing location of the slope versus the change in absorbance in a solution of various pHs at 257.0, 281.0, 292.5, 366.5, and 384.5 nm, respectively (Fig. 9). The potentiometric titration curve of **1** also suggested that **1** has another p*K*a at around pH 11 (Fig. 5).

During the solvent extraction for alkali metal species using **1**, the maximum extraction for Li^+ at pH 11 was confirmed and not the extraction of Na^+ and K^+ (Fig. 10). It has been reported that for the same solvent extraction using a calix[4]arene consisting of four *p*-(1,1,3,3-tetramethyl)butylphenols, the extraction of the three alkali metal species was not observed at pH 9.7 (for Na^+, an extraction of only 2% was observed) [14].

The electrochemical properties of **1** in comparison to *p-tert*-butylphenol and phloroglucinol were investigated by cyclic voltammetry in DMF in the presence of 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) as the supporting electrolyte using a Pt working electrode and a Ag/Ag^+ reference electrode at ambient temperature (Fig. 10) [19]. The calix[4]arene **1** displayed one pair of redox waves. A comparison of the redox potentials reveals that the oxidation potential of **1** is almost the same as that of phloroglucinol, while *p-tert*-butylphenol gave no oxidation potential. These results show that **1** has the oxidation potential of the corresponding two phloroglucinols.

In conclusion, based on the analyses of the ^1H and ^{13}C NMR, and UV–vis spectra of **1** under alkaline conditions (> pH 11), it was suggested that the two phloroglucinol moieties of **1** changed to the keto-forms and simultaneously the ring-structure of **1** changed from the corn-type in which four hydroxyl groups are strongly hydrogen-bonded, to the other types. For the behavior of **1**, it showed a selective solvent extraction of a maximum 15% for Li^+ at pH 11, among the alkali metal ions (Li^+, Na^+, and K^+), and gave a redox potential due to the two phloroglucinols.

EXPERIMENTAL

The solvents used in this reaction were prepared by distillation. For separation and purification, flash-column chromatography was performed on silica-gel (230–400 mesh, Fuji-Silysia Co., Ltd., BW-300). Melting points were determined using a Stuart Scientific (UK) SMP-3 melting point apparatus and are uncorrected. The electron spectra were measured using a Hitachi U-3000 spectrophotometer. The IR measurements were achieved using a Horiba FT-720 IR spectrometer. The NMR spectra were recorded

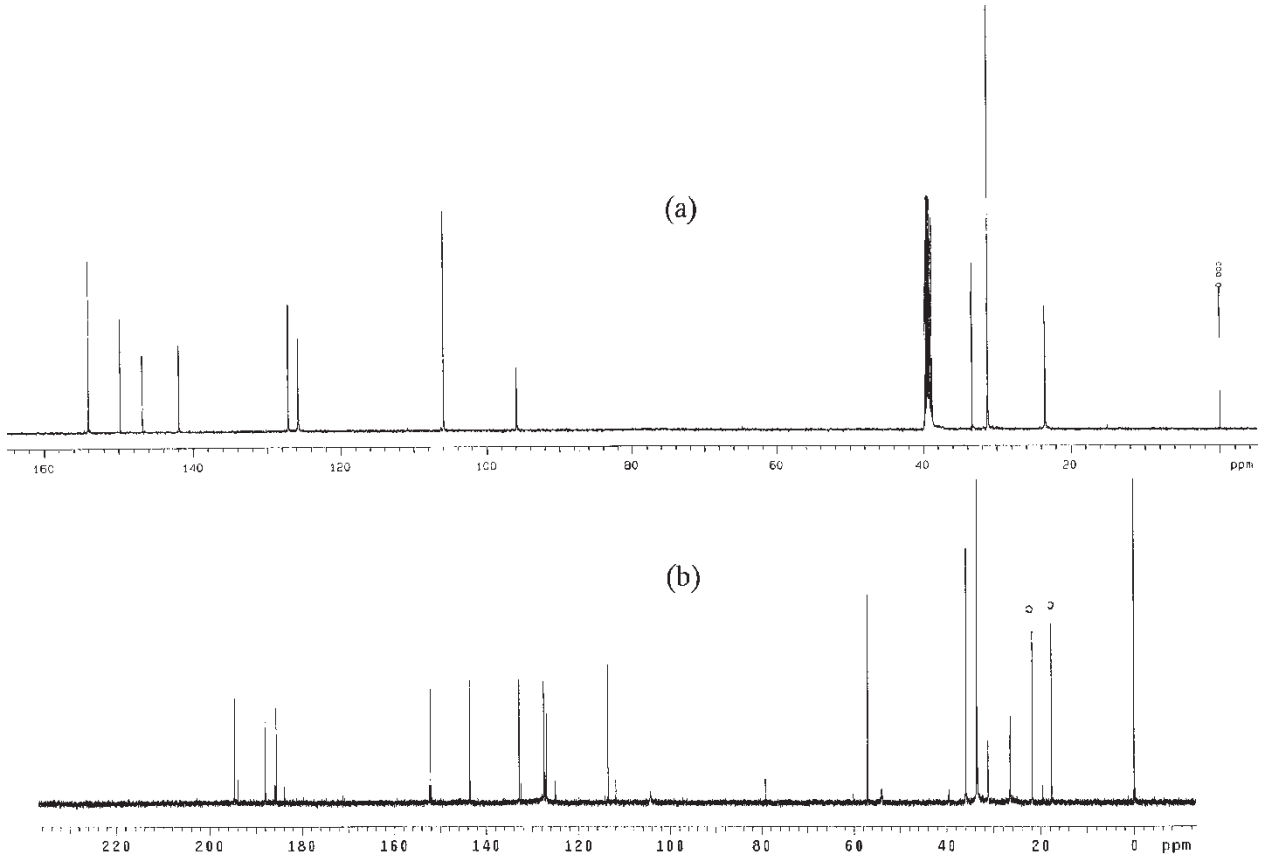


FIGURE 4 ^{13}C NMR spectra of **1**, (a) in DMSO-d_6 and (b) in NaOD–D_2O solution (pH 12.8).

on an Inova 500 spectrometer using Me_4Si and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as the internal standard. The mass spectral data were obtained by FAB using 3-nitrobenzyl alcohol (NBA) as the matrix on a JEOL JMS-AX505HA mass spectrometer. Elemental analyses were performed using a Perkin-Elmer PE 2400 II instrument. The pH was measured using a Horiba N-8F pH meter. For the extraction of the alkali metal species, alkali metal ions were measured by a Hitachi Z-5010 atomic absorption spectrometer or a Shimazu ICPS-7000 emission spectrometer. The cyclic voltammogram was obtained using a conventional three-electrode system on a Model CS-1090 computer-controlled electroanalytical system from Cypress Systems (Lawrence, KS, USA).

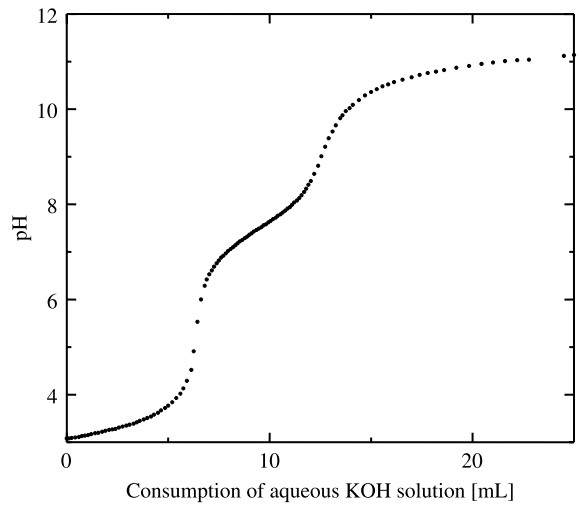


FIGURE 5 Potentiometric titration of **1**.

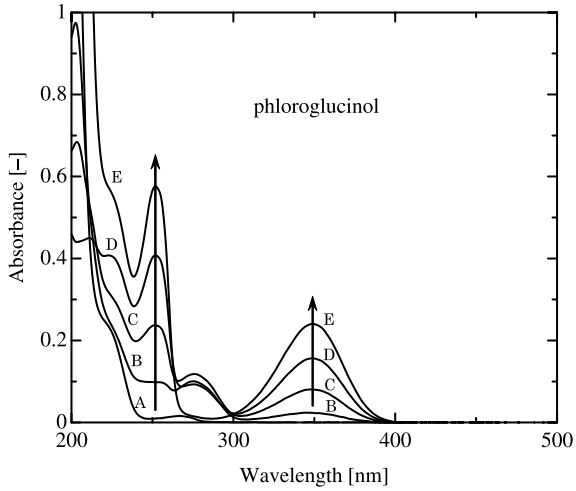


FIGURE 6 Absorption spectra of phloroglucinol at pH 2.96 (A), 8.80 (B), 9.20 (C), 9.60 (D), and 12.00 (E).

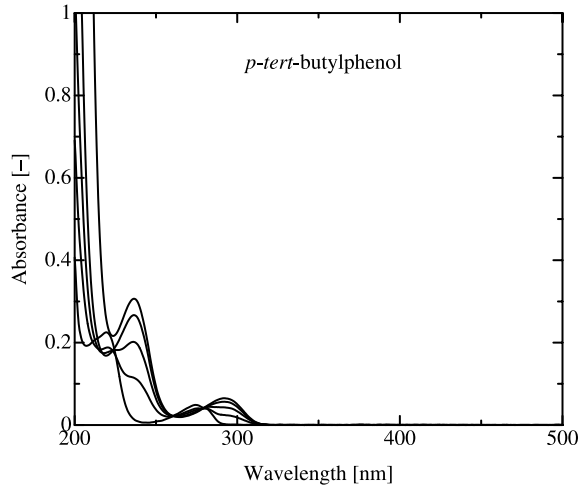


FIGURE 7 Absorption spectra of *p-tert*-butylphenol at pH 2.96 (A), 10.00 (B), 10.50 (C), 11.00 (D) and 12.00 (E).

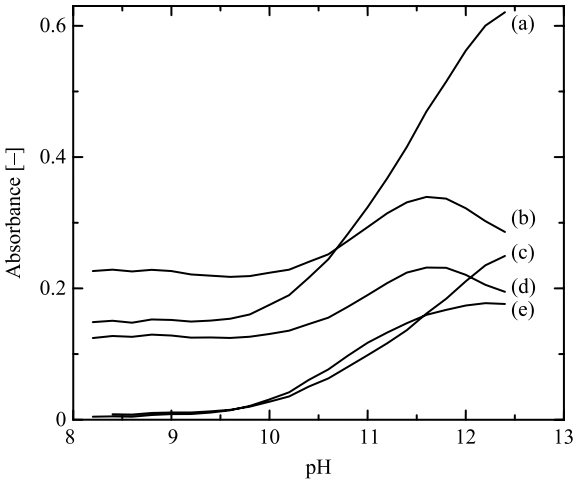


FIGURE 9 Spectrometric pH titration of **1** at 257.0 (a), 281.0 (b), 292.5 (c), 366.5 (d) and 384.5 (e) nm.

2,6-Bis(2′,4′,6′-trimethoxybenzyl)-4-*tert*-butylphenol (4)

To a stirred solution of **2** (9.6 g, 57.1 mmol) and *p*-TsOH·H_2O (0.272 g, 1.43 mmol) in dry toluene (5 mL), a solution of **3** (3.0 g, 14.3 mmol) in dry toluene (15 mL) was dropwise added at 40°C for periods up to 1 h under argon. The resulting mixture was further stirred at 60°C for 4 h. After cooling, to the reaction mixture was added a 5% $NaHCO_3$ aqueous solution and then extracted twice by AcOEt. The combined organic layer was washed with brine and dried over anhydrous Na_2SO_4. After removing the organic solvents, the residue was purified by silica-gel column chromatography. The crude product was recrystallized from toluene to give **4** (4.15 g, 57%) as colorless prisms.

Colorless prisms (toluene). Mp 148–150°C. IR (KBr) cm^{-1}: 3429, 2996, 2954, 2837, 1612, 1595, 1207, 1122, 813. ^1H NMR ($CDCl_3$) δ: 1.14 (9H, s, *tert*-butyl), 3.80 (12H, s, 2′,6′-OMe × 2), 3.81 (6H, s, 4′-OMe), 3.87 (4H, s, CH_2 × 2), 6.16 (4H, s, 3′,5′-ArH × 2), 6.90 (2H, s, 3,5-ArH), 7.41 (1H, s, OH). FAB-MS (*m*/*z*) 511 $(M + H)^+$. Anal. Calcd for $C_{30}H_{38}O_7$: C, 70.56; H, 7.50. Found: C, 70.68; H, 7.66.

5,17-Di-*tert*-butyl-26,28-dihydroxy-10,12,22,24,25,27-hexamethoxycalix[4]arene (5)

To a refluxing solution of *p*-TsOH·H_2O (56.8 mg, 0.30 mmol) in dry toluene (900 mL), a solution of the trimer **4** (1.00 g, 1.96 mmol) and **3** (0.411 g, 1.96 mmol) in dry toluene (600 mL) was added dropwise for 9 h. The water was removed with a Dean-Stark trap. After additional refluxing for 1 h, the reaction mixture was cooled and then the toluene was removed under vacuum to 200 mL. The residual mixture was washed with a 5% $NaHCO_3$ aqueous

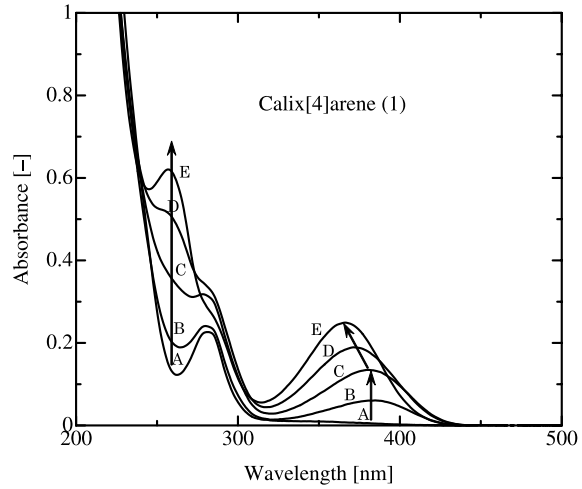


FIGURE 8 Absorption spectra of **1** recorded at pH 8.18 (A), 10.40 (B), 11.20 (C), 11.80 (D) and 12.40 (E).

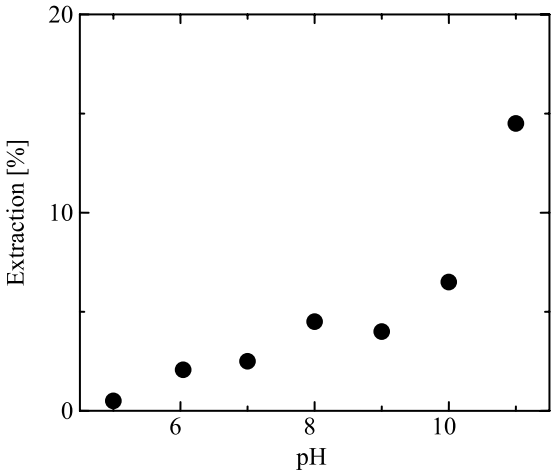


FIGURE 10 Effect of pH on the extraction of Li^+.

solution and water, and then dried over anhydrous Na_2SO_4. After removing the toluene, the residual syrup was separated by silica-gel column chromatography (1st: *n*-hexane-AcOEt = 5:1, 2nd: $CHCl_3$) to give the crude **5**, which was recrystallized from $CHCl_3$ to give **5** (0.496 g, 37%) as colorless prisms.

Colorless prisms ($CHCl_3$). Mp > 365°C. IR ν (KBr) cm^{-1}: 3400, 2960, 2836, 1600, 1485, 1201, 1122, 1087. ^1H NMR ($CDCl_3$) δ: 1.23 (18H, s, 5- and 17-*tert*-butyl), 3.64 (4H, d, $J = 12.5$ Hz, $CH_2 \times 4$), 3.71 (12H, s, 10-,12-,22-, and 24-OMe), 3.93 (4H, d, $J = 12.5$ Hz, $CH_2 \times 4$), 3.94 (6H, s, 25- and 27-OMe), 6.05 (2H, s, 11- and 23-ArH), 7.97 (2H, s, 26- and 28-OH). ^{13}C NMR ($CDCl_3$) δ: 25.4 (CH_2), 31.7 (*tert*-butyl CH_3), 33.7 (*tert*-butyl quaternary C), 63.5 (OMe), 91.7 (C11,23), 114 (C-1,9,13,21), 126.7 (C-4,6,15,19), 141 (C-5,17), 151 (C-26,28), 155 (C-25,27), 157 (C-10,12,22,24). FAB-MS (m/z) 685 $(M + H)^+$. Anal. Calcd for $C_{42}H_{52}O_8 \cdot 0.5CHCl_3$: C, 70.56; H, 7.75. Found: C, 70.68; H, 7.66. Solubility: soluble; toluene, $CHCl_3$. Sparingly soluble; DMSO, AcOEt. Insoluble; MeOH, H_2O.

5,17-Di-*tert*-butyl-10,12,22,24,25,26,27,28-octahydroxycalix[4]arene (1)

To a stirred solution of **5** (1.0 g, 1.46 mmol) in dry CH_2Cl_2, BBr_3 (11.0 g, 44.0 mmol) was added at −78°C under argon. The reaction mixture was stirred at room temperature for 1 d, and then quenched with a saturated $NaHCO_3$ aqueous solution then extracted three times with AcOEt. The organic layer was dried over anhydrous Na_2SO_4 and evaporated under vacuum. The residue was purified by silica-gel column chromatography (*n*-hexane-AcOEt = 2:1). The crude product was recrystallized from $CHCl_3$ to give **1** (0.755 g, 86.2%) as colorless prisms

Colorless prisms ($CHCl_3$). Mp > 365°C. UV−vis λ_{max} nm (ε): MeOH: 283 (8.2×10^3), buffer (pH 8): 285 (1.0×10^4), (pH 10): 279 (1.1×10^4) and 383 (4.3×10^3), (pH 11): 376 (7.8×10^3), (pH 12): 256.5 (2.5×10^4) and 367.5 (1.1×10^3); IR ν (KBr) cm^{-1}: 3400, 3240, 2962, 1622, 1485, 1446, 1170, 1111, 1037, 821; ^1H NMR (DMSO-d_6) δ: 1.15 (18H, s, *tert*-butyl x 2), 3.66 and 3.69 (each 4H, br. s, $CH_2 \times 4$), 5.94 (2H, s, H-11 and 23), 7.23 (4H, s, H-4, 6, 16, and 18), 9.20 (4H, s, H-25, 26, 27, and 28), 9.88 (4H, br. s, H-10, 12, 22, and 24); ^{13}C NMR (DMSO-d_6) δ: 23.5 (CH_2), 31.2 (CH_3), 33.4 (*tert*-butyl quaternary C), 95.9 (C-11 and 23), 106.0 (C-1, 9, 13, and 21), 125.8 ((C-4, 6, 16, and 18), 127.2 (C-3, 7, 15, and 19), 141.9 (C-5 and 17), 146.9 (C-25 and 27), 149.8 (C-26 and 28), 154.1 (C-10, 12, 22, and 24); Assignment of each signal at 146.9 and 149.8 ppm may be exchanged. FAB-MS (m/z) 601 $(M + H)^+$; ^1H NMR (50 mg in D_2O with 30 μL of 40 wt% NaOD, and 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt as the internal standard, pH 12.8) δ: 1.06 (18H, s, *tert*-butyl), 2.80 (2H, d, $J = 13.7$ Hz, CH_2), 3.11 (2H, d, $J = 13.5$ Hz, CH_2), 3.33 (2H, d, $J = 13.5$ Hz), 3.79 (2H, d, $J = 13.7$ Hz, CH_2), 6.74 (2H, d, $J = 2.3$ Hz, ArH), 7.00 (2H, d, $J = 2.3$ Hz, ArH); ^{13}C NMR (the same sample as that of ^1H NMR) δ: 26.36 (s), 31.05 (s), 31.18 (s), 33.47 (t), 33.50 (t), 35.79 (q), 53.88 (t), 104.23 (q), 113.48 (q), 126.76 (t), 126.90 (t), 127.28 (t), 127.46 (t), 132.71 (q), 143.51 (q), 151.95 (q), 185.54 (q), 187.90 (q), 194.50 (q). FAB-MS (m/z) 601 $(M + H)^+$. Anal. Calcd for $C_{36}H_{40}O_8 \cdot 0.1CHCl_3$: C, 70.83; H, 6.59. Found: C 70.77; H, 6.93. Solubility: soluble; AcOEt, MeOH, DMSO. Sparingly soluble; Et_2O, $CHCl_3$. Insoluble; H_2O.

Potentiometric Titration

An aqueous methanol solution of **1** (60 mg/110 mL, MeOH:H_2O = 60:50) was adjusted the pH to **3** with 2 M HCl. To this solution was separately added 0.1–0.6 mL of a KOH aqueous solution (8.88×10^{-2} mol/l), and the pH of the resulting mixture was measured with a pH meter. As shown in Fig. 2, it was observed that **1** dissociated a proton at pH 3–4 and 7.5, respectively. Dissociation at pH 3–4 was not clear because a small amount of 2 M HCl was initially added to the aqueous methanol solution of **1** in order to adjust the pH to 3.0.

Spectrometric pH Titration

The change in the UV−vis spectrum of phloroglucinol, *p-tert*-butylphenol, and **1** at various pHs was measured (Figs. 6–8). The UV−vis spectra of the 5% methanolic aqueous solution of phloroglucinol and *p-tert*-butylphenol were measured for each 0.5 rise from pH 3 by the addition of an aqueous KOH solution. Calix[4]arene **1** (20 mg) was dissolved in 20 mL of methanol and up to 200 mL with a buffer (A: 0.2 M H_3BO_4 + 0.2 M KCl, B: 0.1 M NaH_2PO_4, pH 8.0) (3.3×10^{-5} M). This 10% methanolic buffer (pH 8.0) solution of **1** was measured for each pH 0.5 rise by the addition of an aqueous KOH solution, because the 10% methanolic acidic solution of **1** (pH < 6) precipitated. However, the change in the UV−vis spectrum under acidic conditions (pH < 7) using a 100% methanol solution of **1** was not observed. Based on these results, it is estimated that one or more phenolic hydroxyls have already dissociated at pH 6 in the 10% methanolic buffer solution of **1**. This result is analogous to the potentiometric titration (pKa = 3–4 and 7.5) results.

Solvent Extraction of Alkali Metal Ions with Calix[4]arene (1) (Fig. 10)

The pH of the aqueous phase was adjusted with succinic acid-NH_3 (pH 5.0), MES-NH_3 (pH 6.0–7.0), Tris-HNO_3 (pH 8.0), CHES-NH_3 (pH 9.0–10.0), or NH_4Cl-NH_3 (pH 11.0). In this study, the metal species Li^+, Na^+, and K^+ were prepared as the solutions of LiCl, NaCl, and KCl in water, respectively. A buffer solution (5 mL) including

a metal ion (1.0×10^{-4} M) and a solution (5 mL) of **1** in nitrobenzene (1.0×10^{-3} M) were mixed and shaken for 12 h. After centrifuging (3000 rpm × 10 min), 4 mL of conc. HNO_3 was added to 4 mL of the aqueous phase separated from the organic phase and then heated for several hours at 130–150°C until the disappearance of the organic materials. The residual salts were dissolved in conc. HNO_3 and then diluted to 10 mL with water. The total concentration of the metal species remaining in the aqueous phase, $[M]_{aq}$, was determined by the value measured for the metal ion in the above prepared 10 mL using an atomic absorption spectrometer or an emission spectrometer.

Extraction efficiency:

$$E\% = ([M]_T - [M]_{aq})/[M]_T \times 100$$

$[M]_T$: concentration of the metal species remaining in the aqueous phase after extraction by only nitrobenzene. $[M]_{aq}$: concentration of the metal species remaining in the aqueous phase after extraction by nitrobenzene solution of **1**.

Measurement of Cyclic Voltammogram of 1, *tert*-Butylphenol, and Phloroglucinol (Fig. 11)

Separate 10 mM solutions of **1**, *p-tert*-butylphenol, and phloroglucinol in DMF were prepared. Cyclic voltammograms were obtained using a conventional three-electrode system on a Model CS-1090 computer-controlled electroanalytical system of Cypress Systems (Lawrence, KS, USA). For the electrochemical measurements, a platinum wire electrode was used as the working electrode. A platinum wire served as the counter electrode. A silver wire (Ag/Ag^+) was used as the reference electrode (BAS, Tokyo). These electrodes were first polished using a 15-mm diamond polish followed by a 0.3 mm α-alumina paste for 15 min. After being washed with water, dilute HCl and water, the electrodes were immediately used. All the solutions were purged prior to the electrochemical measurements using nitrogen gas. The voltages measured with respect to Ag/Ag^+. The scan rate was 50 mV s^{-1}.

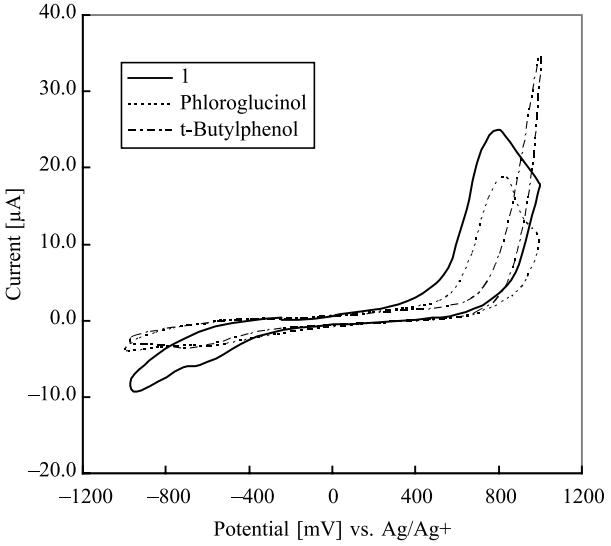


FIGURE 11 Cyclic voltammogram of **1**, phloroglucinol, and *p-tert*-butylphenol in DMF on a platinum electrode; c = 1.0×10^{-2} M, scan rate: 50 mV s^{-1}, base electrolyte: *TBAP*, 0.1 M.

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