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Chromened *t*-butylcalix[4]arenes: cooperation effect of chromene and calixarene moieties on photochromism and metal-ion binding ability

Saleh A. Ahmed,[a,†] Mutsuo Tanaka,[a,*] Hisanori Ando,[a] Hitoshi Iwamoto[b] and Keiichi Kimura[b,*]

[a]*Special Division for Human Life Technology, AIST Kansai, 1-8-31, Midorigaoka, Ikeda, Osaka 563-8577, Japan*
[b]*Department of Applied Chemistry, Faculty of Systems Engineering, Wakayama University, 930, Sakae-dani, Wakayama, Wakayama 640-8510, Japan*

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Abstract—Novel *t*-butylcalix[4]arenes bearing several chromene molecules were synthesized, and their photochromism and metal-ion binding ability were examined with alkali and alkaline-earth metal ions. While the metal-ion binding ability of the *t*-butylcalix[4]arene moiety facilitated the photoisomerization of the chromene moiety to a great extent, the chromene moiety influenced the metal-ion binding ability of the *t*-butylcalix[4]arene moiety through lariat effect. Therefore, the metal-ion that induced the most facilitated photoisomerization of the chromene moiety was shifted drastically from Li^+ to Ba^{2+} with the increase of the incorporated chromene number. Even without metal ions, the interaction among the chromene moieties derived from the cone-conformation of the *t*-butylcalix[4]arene moiety also facilitated the photoisomerization. © 2003 Elsevier Science Ltd. All rights reserved.

1. Introduction

Calixarenes,[1] which are macrocyclic compounds to form cavities in molecular-sized dimensions, have produced extensive research owing to their potential for the formation of complexes with a variety of guests. While crown ethers are well known to form complexes with metal ions, modified calixarenes can bind with various neutral molecules as well as with metal ions owing to the cavity. A recent intriguing application of calixarenes is a manifold to integrate some functional molecules[2] as the integration of functional molecules could perform alternative function through the cooperation of functional molecules resulting in nonlinear response based on allosteric effect.[3] This phenomenon is ubiquitous in nature, and the appearance of some instances concerning this phenomenon is expected especially in dendrimer chemistry.[4]

Photochromism is a photoinduced reversible phenomenon exhibiting a different absorption spectrum in the visible region by transformation of a photosensitive substrate into another isomer. Photochromic molecules have been a fruitful material because of a large number of their potential applications such as transmission materials and optical switches, memories based on the reversibility.[5] In addition, incorporation of metal-ion recognition moieties to photochromic molecules has been reported to afford a metal-ion responsive photochromic molecule.[6–8] Crown ethers are the most common moiety to induce metal-ion response in photochromic molecules, such as spirobenzopyran,[6] spirooxazine,[7] and chromene.[8]

Although calixarenes show metal-ion binding ability similar to crown ethers, there has been a few reports on a combination of calixarenes with photochromic molecules.[9] In the case of calixarenes, incorporation of several photochromic molecules is possible. Therefore, some interaction not only between the calixarene and the photochromic moieties but also among photochromic moieties is expected to produce additional function when calixarenes adopt the cone conformation to form a rigid cavity, that is, a manifold. This context prompted us to investigate calixarenes bearing several photochromic molecules. We chose chromene as a photochromic moiety to incorporate to the *t*-butylcalix[4]arene skeleton, because chromene is a durable photochromic moiety chemically as well as photochemically.[5a]

In this paper, we report on the photochromism and metal-ion binding ability of the *t*-butylcalix[4]arenes bearing chromene moieties, chromened *t*-butylcalix[4]arenes depending on the cooperation of the chromene and calixarene moieties.

Keywords: chromene; calixarene; photochromism; metal-ion binding.

[*] Corresponding authors. Tel.: +81-72-751-9209; fax: +81-72-751-9629; e-mail: mutsuo-tanaka@aist.go.jp

[†] JSPS Fellow: Permanent Address: Department of Chemistry, Faculty of Science, Assiut University, 71516, Assiut, Egypt.

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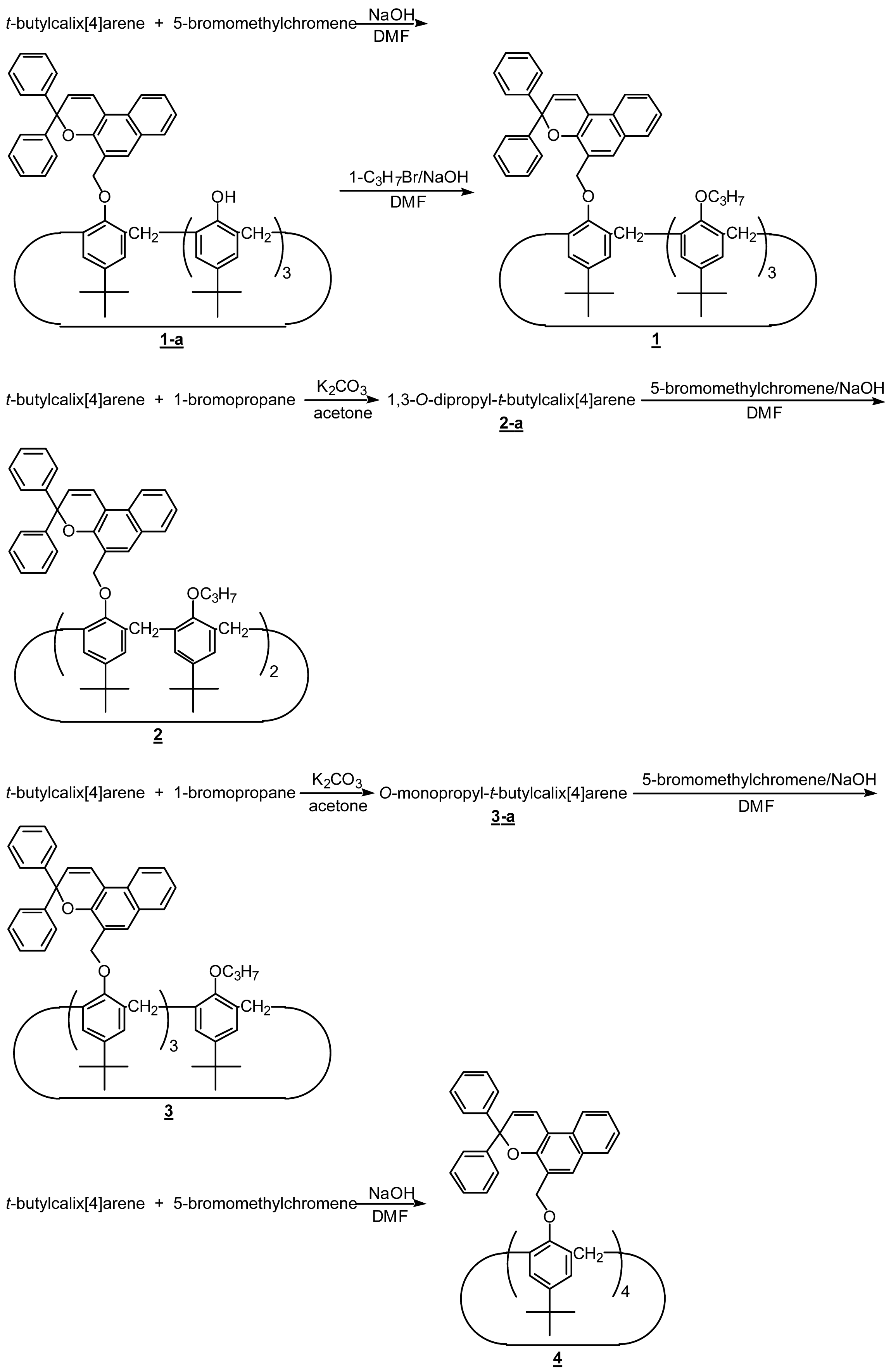


Scheme 1. Preparation outline.

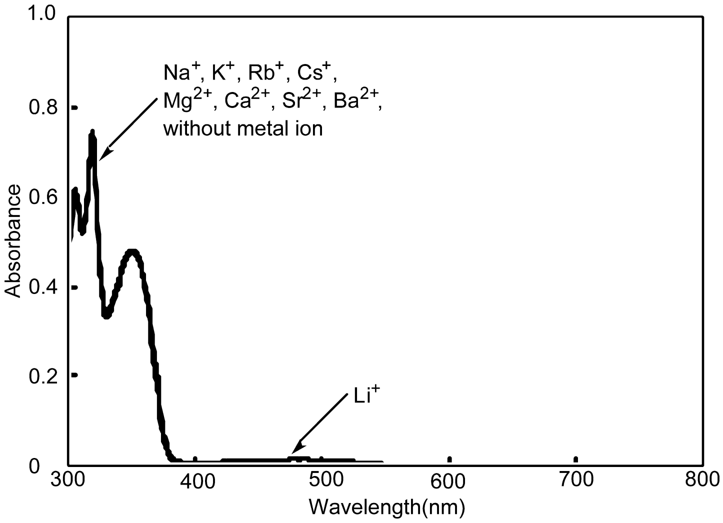


Figure 1. Absorption spectra of **1** before UV irradiation.

2. Results and discussion

2.1. Synthesis

Synthesis of mono-, bis-, tris-, and tetrakis-chromened *t*-butylcalix[4]arenes **1**–**4** was carried out according to the synthetic route outlined in Scheme 1. The reaction of 5-bromomethyl chromene[10] with *t*-butylcalix[4]arene derivatives was undertaken in the presence of sodium hydroxide in dry DMF under a nitrogen atmosphere. In all cases, the products were isolated by GPC (gel permeation chromatography) and obtained in moderate yields. ^{1}H NMR measurements showed that all chromened *t*-butylcalix[4]-arenes took the cone conformation as expected.

2.2. Photochromism of chromened *t*-butylcalix[4]arenes

UV–vis absorption spectra of the chromened *t*-butylcalix[4]arenes were measured in a mixture of acetonitrile and chloroform (7:1 vol.) for **1** or acetonitrile for **2**–**4** in the presence of equimolar amount of a metal perchlorate before and after UV irradiation (365 nm, 3 min) at room temperature.[11] The concentration of the chromene moiety was adjusted to 1×10^{-4} mol dm^{-3} for reasonable comparison. As shown in Figure 1, the spectra of mono-chromened *t*-butylcalix[4]arene **1** were hardly changed by the equimolar amount addition of any metal ions without UV irradiation, but Li^+ induced a slight spectral change. This means that only Li^+ could induce thermal isomerization of the chromene moiety because *t*-butylcalix[4]arene alkylated at the lower rim is known to show a Li^+ binding ability.[1] In the cases of **2**–**4** there was no spectral change in the presence of any metal ions.

Upon UV irradiation (Fig. 2), the Li^+ solution of mono-chromened *t*-butylcalix[4]arene **1** showed the most significant spectral change with a remarkable red-shift,[8,12] and a considerable spectral change was observed in the presence of Na^+. The photoisomerization facilitated by Li^+ is clearly derived from the metal-ion binding ability of the

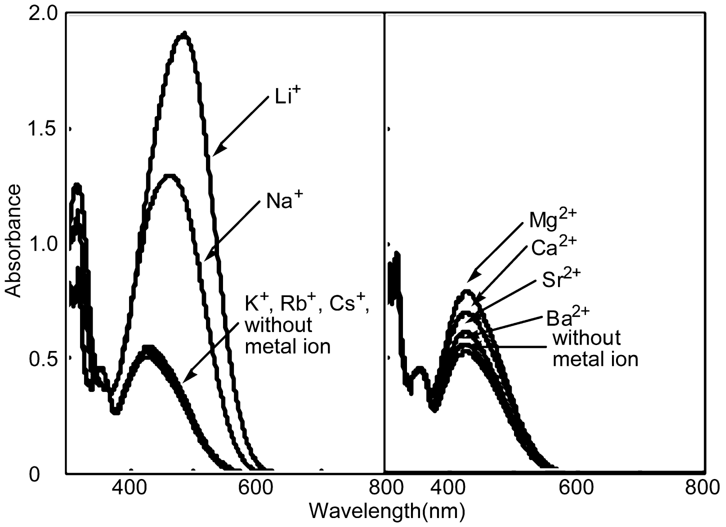


Figure 2. Absorption spectra of **1** under UV irradiation.

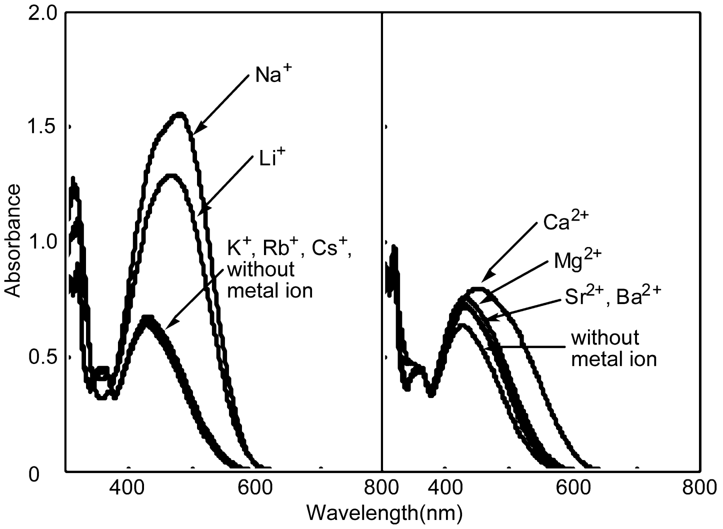


Figure 3. Absorption spectra of **2** under UV irradiation.

t-butylcalix[4]arene moiety. In the case of alkaline-earth metal ions, a little facilitated photoisomerization was induced, but no red-shift was observed. This tendency forms a clear contrast to the crowned chromene where alkaline-earth metal ions induced significant facilitated photoisomerization with red shifts.[8] This contrast is obviously due to the difference between the calixarene and crown ether moieties in metal-ion binding ability.

For bis-chromened *t*-butylcalix[4]arene **2** (Fig. 3), the most significant spectral change was induced by Na^+. This enhancement in the facilitated photoisomerization by Na^+ for **2** compared with that for **1** may be caused by some lariat effect of the chromene moiety. In the presence of alkaline-earth metal ions, Ca^{2+} induced slight facilitated photoisomerization with a red-shift.

The solution of tris-chromened *t*-butylcalix[4]arene **3** (Fig. 4) showed the most significant spectral change in the presence of Na^+ in a similar way to **2**, but the degree of the facilitated photoisomerization induced by Na^+ was smaller than **2**. To the contrary, alkaline-earth metal ions facilitated the photoisomerization of **3** more effectively compared with **2**, and Ca^{2+} induced a considerable spectral change.

Finally for tetrakis-chromened *t*-butylcalix[4]arene **4** (Fig. 5), the most facilitated photoisomerization was observed with K^+ among alkali metal ions, while Sr^{2+} and Ba^{2+} induced significant facilitated photoisomerization.

With increasing the incorporated chromene number, the metal ion inducing the most facilitated photoisomerization changed from Li^+ to K^+ among alkali metal ions. Similar tendency was observed with alkaline-earth metal ions, where the change was from Mg^{2+} for **1** to Ba^{2+} for **4**. This behavior seems to reflect a lariat effect of the chromene moiety as the cavity for metal-ion binding was enlarged with the increase of the incorporated chromene number. On the other hand, the increase of the incorporated chromene number rather resulted in the reduction in the spectral change generally in the case of alkali metal ions. To the contrary, alkaline-earth metal ions facilitated the

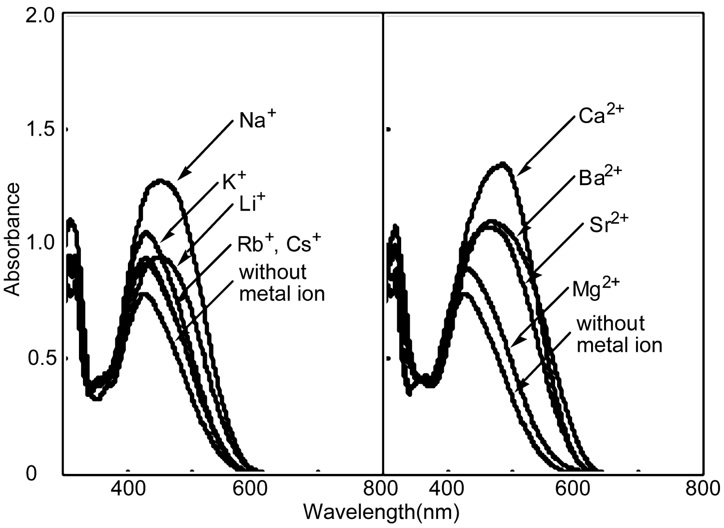


Figure 4. Absorption spectra of **3** under UV irradiation.

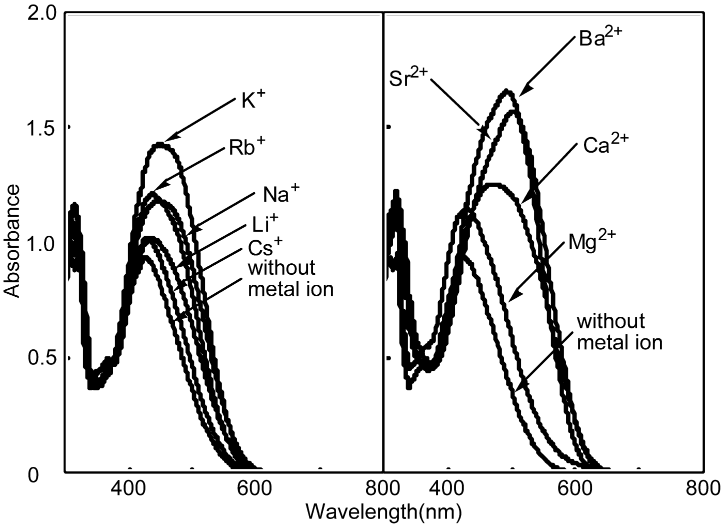
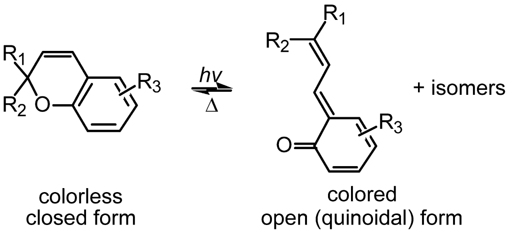


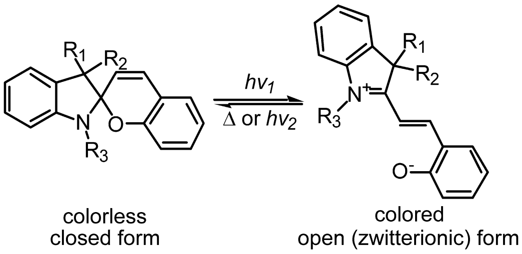
Figure 5. Absorption spectra of **4** under UV irradiation.

photoisomerization more effectively with the increase of the incorporated chromene number. Upon UV irradiation, it has been reported that chromene is converted to the quinoidal form as shown in Scheme 2.[13] The molar extinction coefficient (λ=483 nm) of the quinoidal form for **1** in the presence of Li^+ was evaluated as 2.1×10^4. Therefore, the molar ratio of the converted chromene moiety to the quinoidal form for **1** under UV irradiation was estimated as 91 and 27% in the presence of Li^+ and Ba^{2+}, respectively. Similarly, the molar ratio of the converted chromene moiety to the quinoidal form for **4** was estimated 49 and 79% in the presence of Li^+ and Ba^{2+}, respectively. This indicates that the stoichiometry of the quinoidal form per Li^+ and Ba^{2+} increased to 1.96 from 0.91 and to 3.16 from 0.27 with the increase of the incorporated chromene number, respectively. This tendency clearly shows that Ba^{2+} facilitates the photoisomerization more effectively than Li^+ with increasing the incorporated chromene number. It is well known that calix[4]arenes possess the binding ability to alkali metal ions[1] while the carbonyl group is an effective functional group to promote the binding to alkaline-earth metal ions.[14] Therefore, this tendency seems to be derived from the difference in metal-ion binding ability between the *t*-butylcalix[4]arene and the carbonyl group of chromene moieties.

It has been recognized that the open form of spirobenzopyran is significantly stabilized by aggregation through electrostatic interaction[15] because the open form of spirobenzopyran tends to adopt the zwitter ionic form with significant polarity (Scheme 3).[16] Although the open form of chromene, the quinoidal form, does not have significant polarity compared with the zwitterionic form, some stabilization effect due to polarity is expected. To evaluate stabilization effect for the open form through interaction among the chromene moieties, absorption spectra for **1**–**4** under UV irradiation in the absence of a metal ion were summarized in Figure 6. For comparison, the concentration of chromene moiety was adjusted to 1×10^{-4} mol dm^{-3} for all solutions. The photoisomerization of the chromene moiety was clearly more facilitated with the increase of the incorporated chromene moiety number. This suggests some interaction among the chromene moieties to produce polar atmosphere.



Scheme 2. Photoiomerization of chromene.



Scheme 3. Photochromism of spirobenzopyran.

Calixarenes have possibility to form 1:2 complex with metal ions when the cavity of calixarenes is large enough. Therefore, the stoichiometry of the metal-ion complexes of chromened *t*-butylcalix[4]arenes was examined by Job plot. Job plots for bis- and tetrakis-chromened *t*-butylcalix[4]arenes with Na^+ and K^+ showed a maximum absorption peak around 0.5 exhibiting 1:1 complex stoichiometry.

2.3. Stabilization effect of metal ions on quinoidal form

In order to evaluate stabilization effect of metal ions on the quinoidal form of the chromened *t*-butylcalix[4]arenes, we determined thermal decoloration rate constants in a similar fashion as reported previously.[11] The smaller decoloration rate constants mean the higher stabilization effect on the

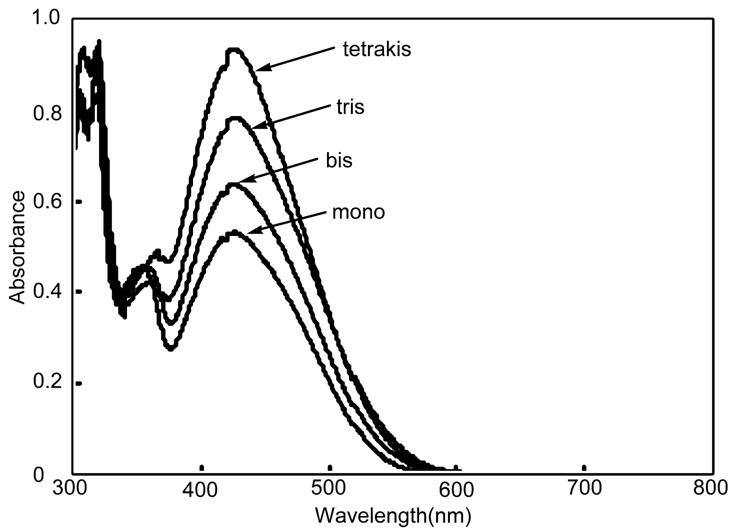


Figure 6. Absorption spectra of **1**–**4** under UV irradiation in the absence of metal ion.

Table 1. Decoloration rate constants (10^{-2} s^{-1})

	Without metal ion	Li^+	Na^+	K^+	Rb^+	Cs^+	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}
1	2.4	0.28	1.6	2.5	2.3	2.3	2.0	2.1	2.5	2.3
2	2.0	1.1	0.20	1.6	1.7	1.9	1.5	0.62	1.5	1.8
3	1.9	1.5	0.54	1.6	1.6	1.6	1.7	0.29	0.83	0.44
4	2.0	1.6	0.71	0.59	1.0	1.8	1.2	0.32	0.18	0.11

For **1**, a mixture of acetonitrile and chloroform, 7:1 (vol.) was used as a solvent while acetonitrile was used for **2**–**4**.

quinoidal form of the chromened *t*-butylcalix[4]arenes. The rate constants are summarized in Table 1.

Among alkali metal ions, the distinct stabilization effects were observed with Li^+ for **1**, Na^+ for **2** and **3**, and K^+ for **4**. This result implies that a bigger metal ion became favorable to stabilize the open form with the increase of the incorporated chromene number. Similar tendency was observed among alkaline-earth metal ions, and Mg^{2+} for **1**, Ca^{2+} for **2** and **3**, and Ba^{2+} for **4** showed the notable stabilization effects, respectively. This observation clearly indicates that the lariat effect of the chromene moiety changed the metal-ion binding ability of the *t*-butylcalix[4]-arenes depending on the incorporated chromene number. On the other hand, there was no clear difference among the decoloration rate constants in the absence of metal ions. The influence of the interaction among chromene moieties on the stabilization effect, therefore, seems to be smaller compared with the influence of the metal-ion interaction. The tendency in the decoloration rate constants was consistent with that in absorption spectra.

3. Conclusions

The metal-ion binding ability of the chromened *t*-butylcalix[4]arenes to induce the facilitated photoisomerization was drastically shifted from Li^+ to Ba^{2+} with the increase of the incorporated chromene number due to their lariat effect. The interaction among the chromene moieties was also observed to promote the facilitated photoisomerization, but this influence on the facilitated photoisomerization was relatively smaller compared with the interaction of the metal ions.

4. Experimental

4.1. General

All chemicals for synthesis were of available purity and used without further purification. For spectral measurements, spectroscopic grade acetonitrile and chloroform were used as the solvents, while all metal perchlorates were the highest grade available and were employed as received. The procedures for the spectral measurement and the determination of the decoloration rate constants are described in Ref. 11. 5-Bromomethylchromene was prepared according to the methods reported in Ref. 10.

4.1.1. Synthesis of mono-chromened *t*-butylcalix[4]arene 1. For preparation of **1-a**, under nitrogen atmosphere, a dry DMF solution (40 mL) of *t*-butylcalix[4]arene (1.3 g, 2 mmol) and sodium hydroxide pellets (400 mg, 10 mmol) were placed to a three-necked flask and stirred at room temperature until clear solution was obtained (ca. 45 min). To the clear solution, 5-bromomethyl chromene (427 mg, 1 mmol) in dry DMF (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was poured into 5 wt% hydrochloric acid and extracted twice with chloroform. The product of **1-a** obtained by solvent evaporation was purified by GPC (gel permeation chromatography) in 57% yield as white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.20 (36H, m); 3.29

(2H, d, J=13.2 Hz); 3.40 (2H, d, J=13.6 Hz); 4.23 (2H, d, J=13.6 Hz); 4.42 (2H, d, J=13.2 Hz); 5.40 (2H, s); 6.22 (1H, d, J=9.6 Hz); 6.9–7.6 (21H, m); 7.88 (1H, d, J=8.0 Hz); 8.01 (1H, d, J=8.8 Hz); 8.28 (1H, s); 9.43 (2H, s); 10.10 (1H, s); IR (neat, cm^{-1}): 3019 (CH_3); 1215 (PhO); 771 (C=C). Mp 170–171°C.

Under a nitrogen atmosphere, a dry DMF solution (20 mL) of **1-a** (478 mg, 0.5 mmol) and sodium hydroxide pellets (1.2 g, 30 mmol) were placed to a three-necked flask and stirred at room temperature until clear solution was obtained (ca. 30 min). To the clear solution, 1-bromopropane (6.05 g, 50 mmol) in dry DMF (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 17 h. The reaction mixture was poured into 5 wt% hydrochloric acid and extracted twice with chloroform. The product of **1** obtained by solvent evaporation was purified by GPC in 62% yield as orange solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.54 (6H, t, J=7.4 Hz); 0.837 (9H, s); 0.839 (9H, s); 0.99 (3H, t, J=7.4 Hz); 1.34 (18H, s); 1.7–2.0 (6H, m); 3.02 (2H, d, J=12.8 Hz); 3.08 (2H, d, J=12.4 Hz); 3.60 (2H, t, J=7.2 Hz); 3.8–4.0 (4H, m); 4.38 (2H, d, J=12.4 Hz); 4.57 (2H, d, J=12.4 Hz); 5.01 (2H, s); 6.29 (1H, d, J=10.0 Hz); 6.45 (4H, s); 7.0–7.5 (17H, m); 7.76 (1H, d, J=8.0 Hz); 7.97 (1H, d, J=8.8 Hz); 8.17 (1H, s); IR (neat, cm^{-1}): 3019 (CH_3); 1210 (PhO); 786 (C=C); m/z 1120 (M$^+$). Anal. calcd for $C_{79}H_{92}O_5$: C, 84.60; H, 8.27. Found: C, 84.65; H, 8.37. Mp 144–145°C.

4.1.2. Synthesis of bis-chromened *t*-butylcalix[4]arene 2. For preparation of **2-a**, a mixture of *t*-butylcalix[4]arene (1.3 g, 2 mmol) and potassium carbonate (6.9 g, 50 mmol) in acetone (50 mL) was stirred at room temperature under a nitrogen atmosphere for about 40 min. To the mixture, 1-bromopropane (6.15 g, 50 mmol) in 10 mL acetone was added dropwise. The reaction mixture was refluxed for 15 h. The solvent was removed, and the residue was extracted with 5 wt% hydrochloric acid and chloroform. The product of **2-a** obtained by solvent evaporation was purified by GPC in 79% yield as white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.00 (18H, s); 1.26 (6H, t, J=7.0 Hz); 1.27 (18H, s); 1.9–2.1 (4H, m), 3.30 (4H, d, J=13.2 Hz); 3.95 (4H, t, J=6.4 Hz); 4.30 (4H, d, J=12.8 Hz); 6.85 (4H, s); 7.03 (4H, s); 7.85 (2H, s).

Under a nitrogen atmosphere, a dry DMF solution (30 mL) of **2-a** (367 mg, 0.5 mmol) and sodium hydroxide pellets (800 mg, 20 mmol) were placed to a three-necked flask and stirred at room temperature until clear solution was obtained (ca. 30 min). To the clear solution, 5-bromomethyl chromene (854 mg, 2 mmol) in dry DMF (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 15 h. The reaction mixture was poured into 5 wt% hydrochloric acid and extracted twice with chloroform. The product of **2** obtained by solvent evaporation was purified by GPC in 58% yield as pale-orange solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.19 (6H, t, J=7.4 Hz); 0.83 (18H, s); 1.37 (18H, s); 1.6–1.8 (4H, m), 3.01 (4H, d, J=12.8 Hz); 3.91 (4H, t, J=8.4 Hz); 4.53 (4H, d, J=12.8 Hz); 4.95 (4H, s); 6.24 (2H, d, J=9.6 Hz); 6.43 (4H, s); 7.07 (4H, s); 7.1–7.5 (26H, m); 7.61 (2H, d, J=8.0 Hz); 7.94 (2H, d, J=8.4 Hz); 8.11 (2H, s); IR (neat, cm^{-1}): 3019 (CH_3); 1215 (PhO); 776 (C=C); m/z 1424 (M$^+$). Anal. calcd for $C_{102}H_{104}O_6 \cdot H_2O$: C, 84.84; H, 7.40. Found: C, 84.97; H, 7.08. Mp 251–253°C.

4.1.3. Synthesis of tris-chromened *t*-butylcalix[4]arene 3. For preparation of **3-a**, a mixture of *t*-butylcalix[4]arene (1.3 g, 2 mmol), potassium carbonate (552 mg, 4 mmol), and sodium iodide (600 mg, 4 mmol) in acetone (150 mL) was stirred at room temperature under nitrogen atmosphere for about 30 min. To the mixture, 1-bromopropane (123 mg, 1 mmol) in acetone (5 mL) was added dropwise. The reaction mixture was refluxed for 12 h. The solvent was removed, and the residue was extracted with 5 wt% hydrochloric acid and chloroform. The product obtained by solvent evaporation was purified by GPC in 32% yield as white solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.1–1.3 (39H, m); 2.1–2.3 (2H, m); 3.41 (2H, d, J=13.2 Hz); 3.43 (2H, d, J=13.6 Hz); 4.10 (2H, t, J=7.0 Hz); 4.27 (2H, d, J=13.6 Hz); 4.36 (2H, d, J=13.2 Hz); 6.98 (2H, d, J=2.0 Hz); 7.04 (2H, s); 7.05 (2H, d, J=2.0 Hz); 7.09 (2H, s); 9.60 (2H, s); 10.19 (1H, s).

Under a nitrogen atmosphere, a dry DMF solution (30 mL) of **3-a** (230 mg, 0.3 mmol) and sodium hydroxide pellets (400 mg, 10 mmol) were placed to a three-necked flask and stirred at room temperature until clear solution was obtained (ca. 30 min). To the clear solution, 5-bromomethyl chromene (1.28 g, 3 mmol) in dry DMF (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 4 h. The reaction mixture was poured into 5 wt% hydrochloric acid and extracted twice with chloroform. The product of **3** obtained by solvent evaporation was purified by GPC in 46% yield as orange solid: ^{1}H NMR ($CDCl_3$, 400 MHz) δ 0.15 (3H, t, J=7.4 Hz); 0.87 (18H, s); 1.32 (9H, s); 1.34 (9H, s); 1.6–1.8 (2H, m); 2.95 (2H, d, J=12.8 Hz); 3.02 (2H, d, J=12.8 Hz); 4.07 (2H, t, J=8.4 Hz); 4.50 (2H, d, J=12.4 Hz); 4.68 (2H, d, J=12.4 Hz); 5.0–5.2 (4H, m); 5.66 (2H, s); 5.98 (1H, d, J=9.6 Hz); 6.18 (2H, d, J=10.0 Hz); 6.44 (2H, d, J=2.4 Hz); 6.55 (2H, d, J=2.4 Hz); 6.66 (1H, t, J=7.4 Hz); 6.8–7.4 (45H, m); 7.80 (1H, d, J=8.4 Hz); 7.86 (2H, d, J=8.8 Hz); 7.90 (2H, s); 8.57 (1H, s); IR (neat, cm^{-1}): 3019 (CH_3); 1215 (PhO); 769 (C=C); m/z 1730 (M$^+$+2). Anal. calcd for $C_{125}H_{116}O_7 \cdot H_2O$: C, 85.88; H, 6.80. Found: C, 86.17; H, 6.70. Mp 173–174°C.

4.1.4. Synthesis of tetrakis-chromened *t*-butylcalix[4]arene 4. Under a nitrogen atmosphere, a dry DMF solution (30 mL) of *t*-butylcalix[4]arene (65 mg, 0.1 mmol) and sodium hydroxide pellets (120 mg, 3 mmol) were placed to a three-necked flask and stirred at room temperature until a clear solution was obtained (ca. 45 min). To the clear solution, 5-bromomethyl chromene (427 mg, 1 mmol) in dry DMF (10 mL) was added dropwise, and the reaction mixture was stirred at room temperature for 24 h. The reaction mixture was poured into 5 wt% hydrochloric acid and extracted twice with chloroform. The product of **4** obtained by solvent evaporation was purified by GPC in 87% yield as orange solid: ^{1}H NMR

($CDCl_3$, 400 MHz) δ1.07 (36H, s); 2.83 (4H, d, J=12.8 Hz); 4.66 (4H, d, J=12.4 Hz); 5.49 (8H, s); 6.06 (4H, d, J=10.0 Hz); 6.71 (8H, s); 6.79 (4H, t, J=7.8 Hz); 6.87 (4H, d, J=7.6 Hz); 6.9–7.3 (48H, m); 7.80 (4H, d,

J=8.8 Hz); 8.24 (4H, s); IR (neat, cm^{-1}): 3019 (CH_3); 1216 (PhO); 739 (C=C); m/z 2034 (M^++2). Anal. calcd for $C_{148}H_{128}O_8\cdot H_2O$: C, 86.60; H, 6.38. Found: C, 86.24; H, 6.03. Mp 187–189°C.

4.2. Absorption-spectral measurement

A mixture of acetonitrile and chloroform (7:1 vol.) was used as solvent for **1** because of low solubility of **1** to acetonitrile. For **2–4**, acetonitrile was used as solvent. The concentrations of **1–4** were 1×10^{-4}, 5×10^{-5}, 2.5×10^{-5}, and 2.5×10^{-5} mol dm^{-3}, respectively. The absorption spectra for **3** were normalized as the concentration of the chromene moiety was 1×10^{-4} mol dm^{-3} for clear comparison. To evaluate the molar extinction coefficient (λ=483 nm) of the quinoidal form for **1** in the presence of Li^+, various concentrations of Li^+ solutions between 1×10^{-4} and 1×10^{-3} mol dm^{-3} were adopted, and the obtained value 2.1×10^4 was applied to estimate the molar ratio of the converted chromene moiety to the quinoidal form. For the Job plots, the sum concentration of **2** and Na^+ was 1×10^{-4} mol dm^{-3} while that of **4** and K^+ was 5×10^{-5} mol dm^{-3}. The concentrations of Na^+ were 3, 4, 5, 6, or 7×10^{-5} mol dm^{-3}, and that of K^+ were 1.5, 2, 2.5, 3, or 3.5×10^{-5} mol dm^{-3}, respectively.

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