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UV Band Splitting of Chromogenic Azo-Coupled Calix[4]crown upon Cation Complexation

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Calixcrown-6 compounds carrying a pair of phenylazo moieties on the upper rim and two OH groups, one OH group, and two OR groups on the lower rim have been prepared in both the cone and partial cone conformations. UV/vis spectral measurements showed a red shift upon the addition of Ca^{2+} to the calixcrown carrying two OH groups and a blue shift for the calixcrown carrying two OR groups. For the compounds with two OR groups on the lower rim and a fixed partial cone conformation, a blue shift caused by electrostatic interaction between the oxygen atoms of OR and the metal ion as well as a red shift caused by the π-metal complexation between the rotated calix benzene and the metal ion were observed.

Introduction

Calixarenes[1] have been extensively used as hosts for a wide range of metal ions in selective transport,[2] potentiometric,[3] optical,[4] and chromoionophoric system.[5−7] In particular, chromoionophores have long been studied as specific metal ion indicators since Pedersen reported salt-dependent UV measurements for characterizing the complexation processes with crown ethers containing aromatic structure units.[8] Diazo-chromophores bearing the azacrown ether unit were reported to give a color change upon specific metal ion complexation.[9,10] Shinkai et al. reported that calix[4]arene having a 4-(4-nitrophenyl)azophenol unit with three ethyl ester groups showed a lithium ion selectivity with respect to the UV/vis band shift.[11] Chang et al. reported a bathochromic shift of a *p-tert*-butylcalix[4]arene bearing a 1,3-diazophenol unit upon calcium ion complexation.[12] Reinhoudt et al. also reported that a calix[4]arene with triamide and monoalkylated azophenol units on the lower rim gave a UV/vis band shift, in which the direction of the shift was dependent on the conformation of the calixarene.[13] Their research results motivated us to investigate if there are color changes of calix[4]monocrown having a diazophenol unit with mono- and dialkylated compounds upon the metal ion complexation and also to examine if there is any conformational dependence for the wavelength changes. With these questions in mind, we synthesized **1**−**7** and investigated the color change upon the metal ion complexation on the UV/vis spectroscopy.

Results and Discussion

The synthetic routes for **1**−**7** are depicted in Scheme 1. Starting materials **8** and **9** were prepared by adapting published procedures.[14,15] Diazo coupling reaction using *p*-nitrobenzenediazonium tetrafluoroborate and pyridine

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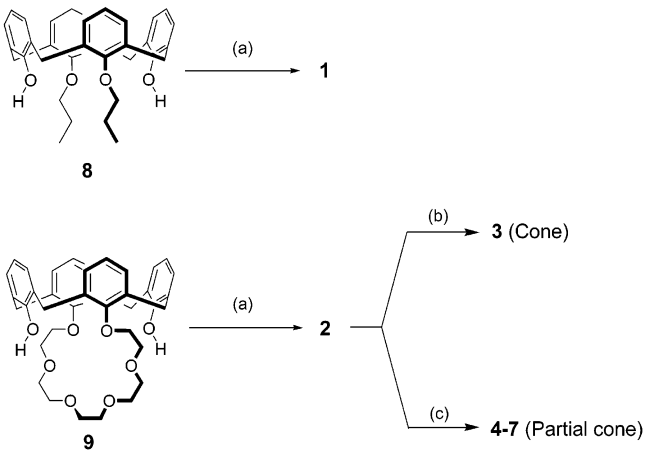
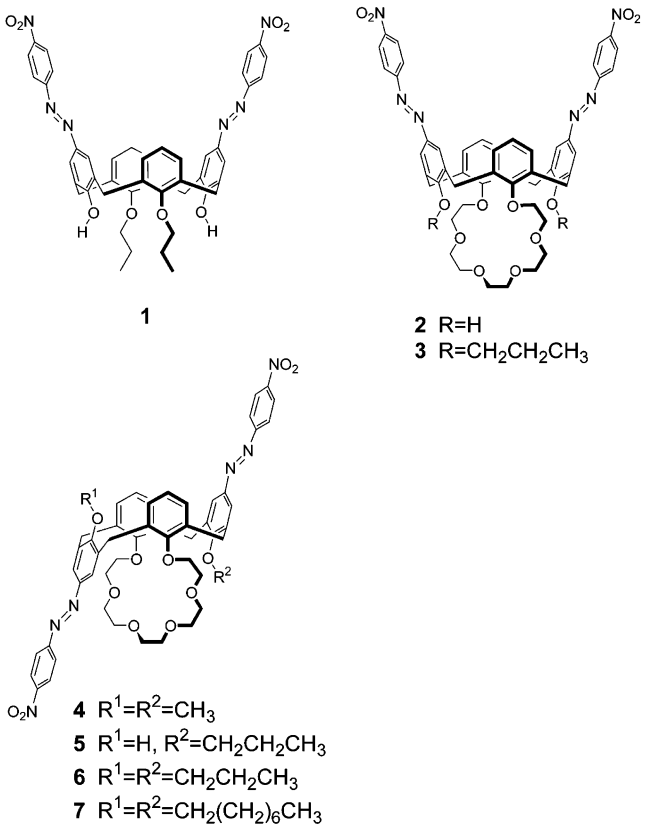
SCHEME 1. Synthetic Scheme for 1−7[a]



[a] Reaction conditions: (a) 4-nitrobenzenediazonium tetrafluoroborate, pyridine, THF; (b) NaH, 1,4-dioxane, reflux for 24∼48 h; (c) K_2CO_3, CH_3CN, 1-iodoalkane, reflux for 24∼48 h.



gave desired products **1** and **2** in moderate yield. For alkylation of **2** with a 1-iodoalkane, reflux for 1−2 days completed the reaction. Conformations of dialkylated compounds were dependent on the base species used. The use of NaH in 1,4-dioxane gave a cone conformer of **3**. When K_2CO_3 was used in acetonitrile, the partial cone conformers of **4**−**7** were solely obtained. The presence of the doublets at around δ 4.3 and 3.5 in the ^{1}H NMR[1a] spectrum and a resonance at about 32 ppm in the ^{13}C NMR[1a] spectrum for compounds **1**−**3** indicated that they possess the cone conformation. For **4**−**7**, two peaks at about 38 and 32 ppm in the ^{13}C NMR spectrum indicated a partial cone conformer (see detailed NMR data in Supporting Information).

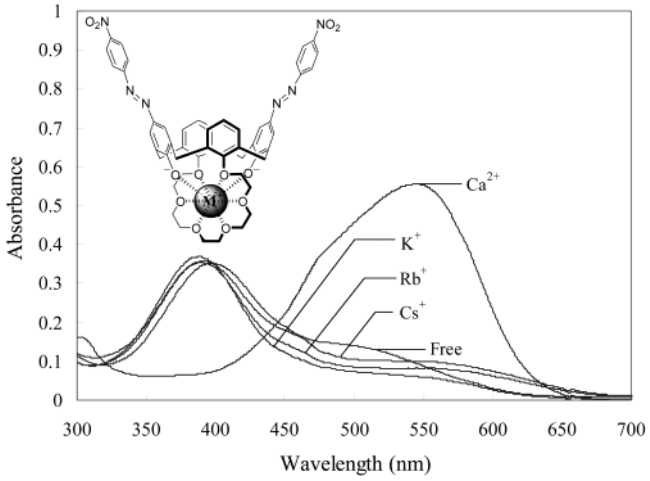


FIGURE 1. Wavelength changes of **2** upon the addition of metal cations. Conditions: **2** (0.01 mM)/CH_3CN; metal cations (10 equiv)/CH_3CN.

To obtain quantitative insight into the metal affinity of the chromogenic calix[4]arene ionophores, we determined the wavelength changes upon complexation of various metal ions. The wavelength changes for **1**−**7** are listed in Table 1. Compound **1** without a crown loop exhibited no change in wavelength upon metal ion complexation because of the lack of a cyclic array to entrap the metal ions. Since 1,3-alternate calix[4]crown-6 compounds are well-known as selective hosts for cesium ion, which can be contained in a highly radioactive waste,[16] we were anxious to determine if the crown units of **2**−**7** play an important role in entrapping cesium ions to produce wavelength changes ($\Delta\lambda_{max}$) in UV/vis spectra. However, neither cesium ion nor other alkali metal ions in this study seemed to be encapsulated in the crown-6 ring, probably because the ligands are not in the 1,3-alternate conformation but in either the cone or partial cone conformation. However, addition of the alkaline-earth metal cations Ca^{2+} into the solution of host **2** gave a marked bathochromic shift from λ_{max} 398 to 548 nm ($\Delta\lambda_{max}$ = 150 nm) as shown in Table 1 and Figure 1. Figure S1 (Supporting Information) shows that titration of Ca^{2+} into a solution of host **2** gave wavelength changes with an isobestic point at 447 nm. Association constants of **2** using a titration method[17] were K_a = 290, 33 095, and 47 640 M^{-1} for Na^+, Mg^{2+}, and Ca^{2+} ions, respectively. For Mg^{2+} and Ca^{2+}, we observed, even with the naked eye, a pronounced color change from red to purple. It is conceivable that even at neutral pH, deprotonation

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TABLE 1. Optical Response of 1−7 (10^{-5} M) to Different Metal Perchlorate Salts (10^{-4} M) in CH_3CN

			metal-induced wavelength changes ($\Delta\lambda_{max}$/nm)[a]								
compd	λ_{max} (nm)	ϵ (cm^{-1} M^{-1})	Li^+	Na^+	K^+	Rb^+	Cs^+	Ag^+	Mg^{2+}	Ca^{2+}	Sr^{2+}
1	392	25 830	0	0	0	0	0	0	0	0	0
2	398	35 240	+111	−10	−10	−10	−9	−6	+145	+150	+74
3	360	43 100	0	−5	0	0	0	0	0	0	0
4	370	29 100	−23	−11	−9	−11	−9	−6	−18	−18	−14
	462	31 800	−2	+2	−4	−4	−4	−6	+10	+10	+9
5	385	43 000	−12	−10	−10	−10	−10	−4	−5	−25	−19
										+129	+102
6	373	28 800	−11	−8	−10	−8	−8	−8	−18	−18	−14
	454	28 500	+10	+5	+3	+2	+2	+6	+19	+18	+17
7	373	36 500	−8	−7	−19	−19	−6	−3	−13	−18	−13
	454	32 500	−41	+5	+2	+2	+2	0	+19	+19	+17

[a] (+) and (−) in wavelength changes denote red and blue shifts, respectively. Samples were prepared by mixing equal volumes of stock solutions of **1**−**7** and the metal perchlorate salts.

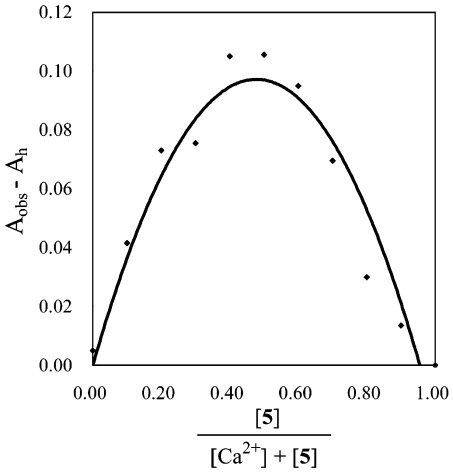

FIGURE 2. Job plot for 1:1 complexation of **5** with Ca^{2+} ion. $\delta A = A_{obs} - A_h$, where A_{obs} and A_h denote the absorbance at 519 nm upon the Ca^{2+} ion complexation and absorbance of free ligand **5**, respectively.

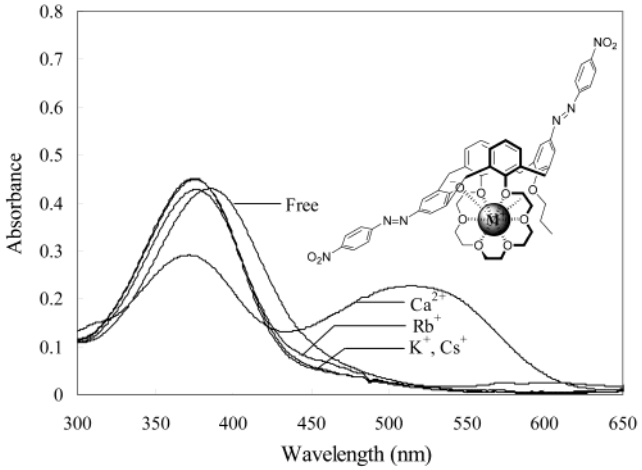

FIGURE 3. Wavelength changes of **5** upon the addition of metal cations. Conditions: **5** (0.01 mM)/CH_3CN; metal cations (10 equiv)/CH_3CN.

of **2** may readily take place because of the assistance of induced metal ions entrapped by the crown loop, causing a charge density shift in the direction of the acceptor substituents (nitro group) of the chromoionophore. In other words, increases in the dipole moments take place, eventually leading to bathochromic band shift.[18]

Cone dipropylated diazo-calix[4]crown **3**, however, did not exhibit a UV/vis band shift upon the metal ion addition as shown in Figure S2 (Supporting Information) probably because the dipropyloxy groups are located in the center of the crown cavity to interrupt the metal ion approach.

Then, we prepared monopropylated diazophenol calix[4]crown-6 (**5**) to investigate the influence of conformation and alkyl group on the wavelength changes in UV/vis spectra. Compound **5** was found to be in the partial cone conformation, in which an unalkylated azophenol group is inverted (proximal) and the other propylated azophenol unit is retained (distal) throughout the ^1H and ^{13}C NMR and two-dimensional NMR investigation. Using just 1 equiv of 1-iodopropane as an alkylating agent, we observed the conformational change from cone to partial cone, in which the unalkylated part was inverted prior to the second alkylation. With this partial cone conformer of **5**, we conducted the Job plotting experiment[17b] to figure out the complexation ratio between **5** and Ca^{2+} ion under the conditions of an invariant total concentration. As a result, the **5**−Ca^{2+} complex concentration approached the maximum when the molar fraction of [**5**]/([**5**] + [Ca^{2+}]) was about 0.5, meaning that it formed a 1:1 complex of **5** and Ca^{2+} as shown in Figure 2.

Like **2**, **5** exhibited a calcium ion selectivity in UV/vis spectra as shown in Figure 3. A hypsochromic shift of 20 nm was observed because the oxygen atoms of the propyloxy units are positively polarized when **5** complexes with the metal ion; then, the excited states are more strongly destabilized by cations than the ground states.[19] For the proximal phenylazo group, the metal ion interacts favorably with the hydroxy unit, which can be easily deprotonated, giving a 129 nm bathochromic shift as explained in the case of **2**−Ca^{2+}. As a result, the proximal azophenol unit seemed to be more tilted toward the inside of the calix[4]arene framework upon metal ion complexation. Figure S3 (Supporting Information) indicates that **5** showing just one band at 385 nm gave a dramatic band splitting caused by hypsochromic and bathochromic shifts with an isobestic point at 440 nm.

Judging from the ^{13}C NMR spectra of **5** (38.2 and 31.2 ppm) and **5**·Ca^{2+} (37.7 and 29.7 ppm), it is certain that

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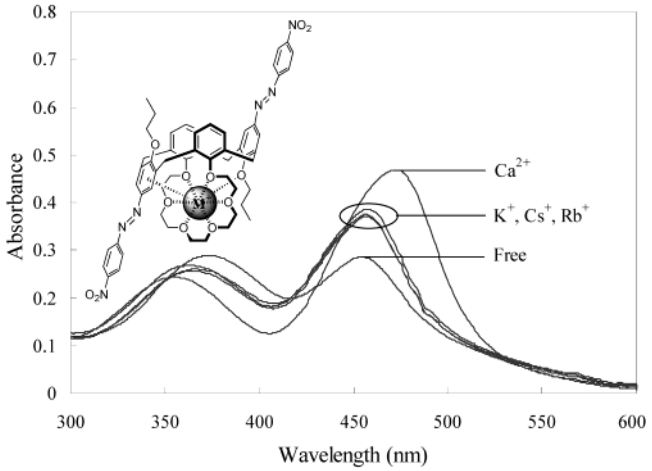

FIGURE 4. Wavelength changes of **6** upon the addition of metal cations. Conditions: **6** (0.01 mM)/CH_3CN; metal cations (10 equiv)/CH_3CN.

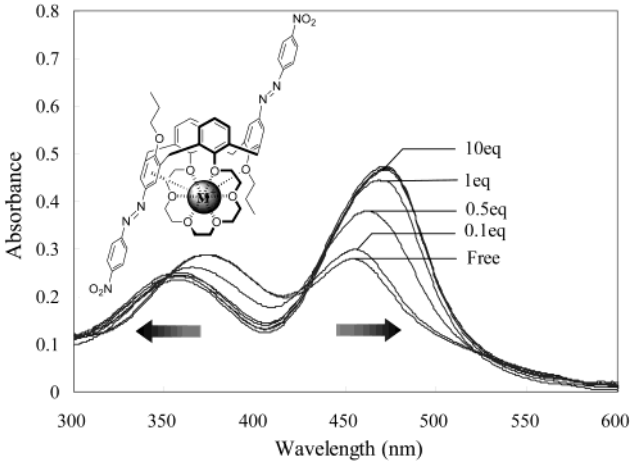

FIGURE 5. Wavelength changes of **6** upon the addition of various amounts of $Ca(ClO_4)_2$. Titration conditions: **6** (0.01 mM)/CH_3CN; $Ca(ClO_4)_2$ (0.1→10 equiv)/CH_3CN.

the partial cone conformation did not change upon the metal cation complexation. From the Ca^{2+} ion-induced chemical shift change of **5** in ^1H NMR spectra (Figure S4, Supporting Information), we could understand that the hydroxyl group of the proximal azophenol takes part in the metal ion complexation. Since the oxygen atom of the propyloxy unit of the distal azophenol coordinates the Ca^{2+} ion, H_a, H_b, and H_c showed an upfield shifts of 0.02, 0.07, and 0.17 ppm, respectively. The chemical shift change patterns are similar to that of **6** (see Figure S5, Supporting Information). It should be noted that a downfield shift for the aromatic hydrogen atoms must occur in ^1H NMR if the aromatic unit of the proximal azophenol unit participates in the π-metal complexation mode (see Figure S5, Supporting Information). In the case of **5**, however, H_d and H_e of the proximal azophenol unit moved not downfield but upfield by 0.09 and 0.25 ppm, respectively, indicating that the phenoxy oxygen atom was involved in the metal cation complexation. Consequently, from both UV and NMR spectroscopy, one can conclude that the hydroxy oxygen atoms of the proximal azophenol unit, the propyloxy oxygen atom, and the crown-6 loop of the partial cone **5** play an important role in Ca^{2+} ion complexation.

Compounds **4**, **6**, and **7** were found to be in the partial cone conformation by the NMR investigation as well. No cone conformer was obtained even in the case of the octyl group (**7**), which is too bulky to rotate through the calix[4]arene framework.[20] This phenomenon occurred because when the diazophenol calix[4]crown-6 was monoalkylated, its conformation changed from the cone into the partial cone conformation before the second alkylation. Interestingly, we found that they have two different UV/vis bands, in which one band at $\lambda_{max} = 454$ nm is for the proximal azophenol and the other band at $\lambda_{max} = 373$ nm is for the distal azophenol unit as shown in Figure 4. Upon the addition of metal cations, the left band moved to blue, while the other band moved to red (Figures 4 and 5). In the partial cone conformation, the Ca^{2+} ion interacted with the propyloxy oxygen atom of the distal azophenyl unit, leading to the 22 nm blue shift, simultaneously interacting with the aromatic ring of the proximal azophenol group by π-metal complexation mode, giving an 18 nm red shift. In consequence, we observed that two bands having different wavelengths separate farther upon the metal ion addition.

To verify these interactions, we also investigated metal ion-induced chemical shift changes in the ^1H NMR spectra as shown in Figure 5S (Supporting Information). Hydrogen atoms of the crown ether ring shifted downfield because of the electrostatic interaction between the oxygen atoms and the Ca^{2+} ions. A singlet peak for H_f shifted downfield by 0.63 and 0.38 ppm, which may be evidence for the π-metal interaction in this system. In addition, H_d and H_e shifted downfield by 0.151 and 0.528 ppm, respectively.

In conclusion, diazo-calixcrown-6 (**2**) in the cone conformation showed a bathochromic shift upon Ca^{2+} ion complexation, while **1** without the crown loop did not show any UV band shift, which implies that the crown ether ring is one of the important factors in the metal ion complexation in this system. For monopropylated diazo-coupled calixcrown-6 (**5**), we found a marked UV band separation, a red and a blue shift. The former is due to the participation of the oxygen atom of the proximal phenyloxy group, and the latter is caused by the oxygen atom of the distal propyloxy group. In the case of dialkylated azophenols (**4**, **6**, and **7**), we observed a hypsochromic band shift driven by an electrostatic interaction between the oxygen atom of the alkyloxy group and the metal cation as well as the bathochromic band shift, which can be explained by the π-metal complexation between the proximal azophenyl group and the metal ion.

Experimental Section

Syntheses. Compound **8** and **9** were prepared in 80−90% yield as described in the literature.[14,15] IR and ^1H and ^{13}C NMR data are given in Supporting Information.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-25,27-bis(1-propyloxy)calix[4]arene (1). A solution of **8** (5.00 g, 9.83 mmol) in THF (300 mL) was treated with 4-nitrobenzenediazonium tetrafluoroborate (4.89 g, 20.66 mmol). The reaction mixture

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was stirred for 30 min at 0 °C, and pyridine was added dropwise. The reaction mixture was stirred for an additional 48 h at 0 °C, treated with 10% aqueous HCl solution (300 mL), and extracted with CH_2Cl_2 (300 mL). The organic layer was washed with 10% aqueous HCl solution (2 × 300 mL) and dried over $MgSO_4$. Removal of the organic solvent in vacuo afforded a reddish solid. Column chromatography using 4:1 $CHCl_3$/hexane as an eluent (R_f = 0.55) on silica gel gave **1** in 23% yield. Mp: 272−273 °C. FAB MS *m*/*z* (M^+): calcd, 806.86; found, 806.31. Anal. Calcd for $C_{46}H_{42}N_6O_8$: C, 68.48; H, 5.21. Found: C, 68.50; H, 5.22.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-25,27-calix[4]-monocrown-6 (2). The procedures are the same as that for **1**. Yield: 38%. Mp: 270−271 °C. FAB MS *m*/*z* (M^+): calcd, 924.95; found, 925.00. Anal. Calcd for $C_{50}H_{48}N_6O_{12}$: C, 64.93; H, 5.19. Found: C, 64.50; H, 5.17.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(1-propyloxy)-25,27-calix[4]monocrown-6, Cone (3). To a mixture of 0.40 g (0.43 mmol) of **2** and 0.17 g (4.32 mmol) of NaH (60% dispersion) in 25 mL of 1,4-dioxane was added dropwise 0.29 g (1.73 mmol) of 1-iodopropane in 5 mL of 1,4-dioxane. The reaction mixture was refluxed for 24 h. After the mixture was cooled to 0 °C, 10 mL of aqueous MeOH was added and the solvent was removed in vacuo. Extraction with 100 mL of 10% HCl solution and 100 mL of CH_2Cl_2 afforded 0.48 g of a red powder. Recrystallization from ether gave **3** as reddish crystals in 55% yield. Mp: 128−130 °C. FAB MS *m*/*z* (M^+): calcd, 1009.11; found, 1008.1. Anal. Calcd for $C_{56}H_{60}N_6O_{12}$: C, 66.60; H, 5.95. Found: C, 66.63; H, 5.91.

General Procedures for Alkylation using K_2CO_3. A solution of **2** (0.54 mmol) in dried acetonitrile (50 mL) was treated with anhydrous K_2CO_3 (10.0 equiv). To this suspension was added an alkylating agent (30.0 equiv) such as 1-iodoalkane, and the reaction mixture was then refluxed for 48 h. After removal of the solvent in vacuo, the residue was acidified with 10% aqueous HCl solution (50 mL) and then extracted with CH_2Cl_2 (50 mL). The organic layer was separated, washed with 10% HCl solution, and dried over anhydrous $MgSO_4$, and the solvent was evaporated to yield a reddish solid. The pure product was isolated by column chromatography using ethyl 2:1 acetate/hexane as an eluent in silica gel.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(methyloxy)-25,27-calix[4]monocrown-6 (4). Yield: 52%. Mp: 170−172 °C. FAB MS *m*/*z* (M^+): calcd, 953.20; found, 953.10. Anal. Calcd for $C_{52}H_{52}N_6O_{12}$: C, 65.55; H, 5.46. Found: C, 65.52; H, 5.42.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-26-mono-(1-propyloxy)-25,27-calix[4]monocrown-6 (5). 1-Iodopropane (1.5 equiv) was used. Yield: 70%. Mp: 149−151 °C. FAB MS *m*/*z* (M^+): calcd, 967.20; found, 968.10. Anal. Calcd for $C_{53}H_{54}N_6O_{12}$: C, 65.83; H, 5.59. Found: C, 65.85; H, 5.55.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(1-propyloxy)-25,27-calix[4]monocrown-6 (6). Yield: 28%. Mp: 153−155 °C. FAB MS *m*/*z* (M^+): calcd, 1009.10; found, 1009.20. Anal. Calcd for $C_{56}H_{60}N_6O_{12}$: C, 66.60; H, 5.95. Found: C, 66.62; H, 5.91.

5,17-Bis[(4-nitrophenyl)(azo)phenyl]-26,28-bis(1-octyloxy)-25,27-calix[4]monocrown-6 (7). Yield: 21%. Mp: 165−167 °C. FAB MS *m*/*z* (M^+): calcd, 1149.30; found, 1149.10. Anal. Calcd for $C_{66}H_{80}N_6O_{12}$: C, 68.93; H, 6.96. Found: C, 68.91; H, 6.99.

Job Plot Experiments

Compound **5** (0.02 mM) in CH_3CN and $Ca(ClO_4)_2$ (0.02 mM) in CH_3CN were prepared as stock solutions. The concentrations of each CH_3CN solution were varied, but their volumes were fixed at 4.0 mL. After the mixture was shaken for 2 h and then centrifuged, the UV/vis absorbance at 519 nm was recorded.

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Supporting Information Available: Additional figures of UV/vis and ^1H NMR spectra (Figures S1−S4) and data of ^1H and ^{13}C NMR and IR (Data S1−S6). This material is available free of charge via the Internet at http://pubs.acs.org.

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