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# Synthesis of novel *p-tert*-butyl-calix[4]arene derivatives and their cation binding ability: chromogenic effect upon side arms binding

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**Abstract**—A series of novel double-armed calix[4]arene derivatives, i.e. 5,11,17,23-tetra-*tert*-butyl -25,27-bis[2-[(2-hydroxy-5-(4-nitroazo)benzylidene)amino]ethoxy]-26,28-dihydroxy-calix[4]-arene (**4**), 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-[(2-hydroxy-5-(2-nitroazo)benzylidene) amino]ethoxy]-26,28-dihydroxycalix[4]arene (**5**), 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-[(2-hydroxy-5-(4-chloroazo)-benzylidene)amino]ethoxy]-26,28-dihydroxycalix[4]arene (**6**), have been synthesized as an selective chromoionophore for $Na^+$. The complexation behavior of ligands **4**-**6** with alkali metal ions $Na^+$, $K^+$, $Rb^+$and $Cs^+$ has been evaluated by using UV–Vis spectrometry in $CH_3CN$–$H_2O$ (99:1/V:V) solution at 25°C. The UV–Vis spectra show that the complexation of **4**-**6** with $Na^+$exhibits obvious bathochromic shifts ($\lambda_{max}$ 379→480 nm) and there is a unique color change in the solution from yellow to red upon complexation. The binding constants for $Na^+$ are higher than that of other alkali metal ions, giving the highest cation selectivity up to 7 for $Na^+/K^+$. The binding ability and photophysical behavior of alkali cations by calix[4]arene derivatives **4**-**6** are discussed from the point of view of substituted effects at the lower rim of parent calix[4]arene and size-fit concept between host calix[4]arenes and guest cations.


## 1. Introduction

Investigations on molecular and/or ionic recognition by calixarenes and their derivatives as synthetic receptors have attracted increasing attention in recent years because of their potential to serve as molecular devices and functional materials.[1–3] One system of current interests is the chromogenic calix[4]arene derivatives, which exhibits selective response to specific metal ions for use as optical sensors. Therefore, structural diverse chromogenic calixarenes have been designed and synthesized for use as selective metal-ion or organic amines chemosenors,[4–12] some of which have been successfully applied in various technologies. Diamond and McKervey have investigated the chromogenic response for lithium by calix[4]arene tetraesters bearing nitrophenol residues, and showed the concentration dependence of the selective chromoionophore for $Li^+$.[7b] Tóth et al. reported the selective binding of sodium ion by azophenol calix[4]arene derivatives.[5b] Recently, Chang and co-workers showed the double dinitrophenylazophenol-armed calix[4]arene-derived diamide and diester to be the highly selective chromogenic ionophores for $Ca^{2+}$.[9a] Böhmer et al. studied the chromoionophore based on calix[5]crown ether, which indicated selectivity for cesium and rubidium ions.[8b] Kubo et al. reported a uranyl ion-selective chromoionophore based on calix[6]arene linked by one indoaniline tether, which could be potentially used as an optical sensor for $UO_2^{2+}$ detection.[6c] However, most of the investigations on selective binding of metal cations by chromogenic calixarene derivatives have been mainly focused on the modified chromoionophores at the upper rim of the parent calixarenes. To the best of our knowledge, the introduction of chromogenic groups to the lower rim of calixarenes has been seen only in the works of Shinkai[4] and of Diamond.[7] Therefore, the scarcity of information in this direction prompted us to undertake the present study.

In our present work, we report the synthesis of bis(azophenol)calix[4]arenes possessing multiple chromogenic donors (Scheme 1) and their cation binding ability for the alkali metal ions $Na^+$, $K^+$, $Rb^+$and $Cs^+$. A simple reason for the selective modification at the lower rim of calixarene is that, the two arms attached to calixarene could provide extra coordination sites to a calix[4]arene platform, and thus can be used as fine-tuned 'basket-type' chromoionophore.[1b] It is of our special interest to examine the chromogenic effects of such modified calixarenes upon complexation with metal cations, which hopefully would provide further guidelines on the design of chromogenic calixarenes possessing the desired properties.

*Keywords*: calix[4]arene derivatives; cations; chromogenic effect; binding constants; spectrometry.
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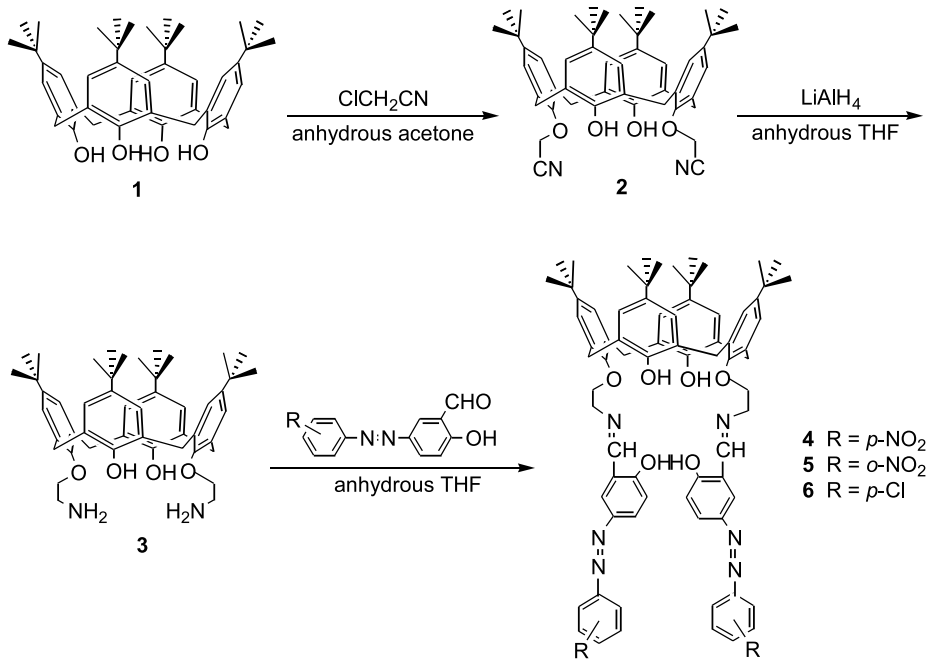


**Scheme 1.**

## 2. Result and discussion

### 2.1. UV spectral titrations

In order to investigate quantitatively the binding ability of the double-arm calix[4]arenes **4**-**6** to the alkali ions $Na^+$, $K^+$, $Rb^+$ and $Cs^+$, spectral titrations were performed in $CH_3CN-H_2O$ (99:1/V:V) solution at 25°C for the calculation of the respective stability constants. In control experiments, the alkali chlorides examined did not show any significant absorption in the spectral range scanned. Typical UV spectral changes upon addition of $Na^+$ to the host **4** in solution are shown in Figure 1. Assuming the 1:1 complex stoichiometry, the inclusion complexation of guest cation (G) with host calix[4]arene derivative (H) is expressed by Eq. (1). The stability constant ($K_S$) of inclusion complex was determined from the gradual changes in absorption intensity ($\Delta A$) upon stepwise addition of G, using a non-linear least squares method.[15]

$$H + G \overset{K_S}{\rightleftharpoons} G{\cdot}H \tag{1}$$

For each host–guest combination examined, the $\Delta A$ values were plotted as a function of $[G]_0$ to give an excellent fit, validating the 1:1 stoichiometry assumed above, as exemplified for the complexation of sodium ion with **4** in Figure 1 (inset). In the repeated measurements, the $K$ value was reproducible within an error of ±5%, which corresponds to an estimated error of 0.15 kJ $mol^{-1}$ in free energy. The complex stability constants ($K_S$) obtained by the curve fitting are listed in Table 1, along with the free energy change of complex formation ($-\Delta G°$). Significantly, the color of the solution changed distinctly from yellow ($\lambda_{max}$=379 nm) to red ($\lambda_{max}$=480 nm) upon addition of

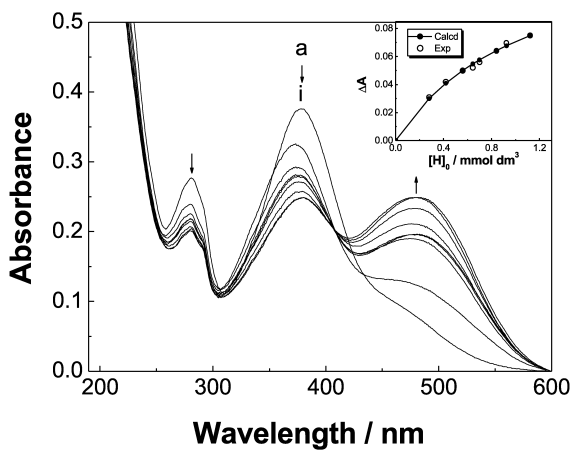


**Figure 1.** UV–Vis spectra of **4** ($0.8\times10^{-5}$ M) in the presence of $Na^+$. The concentration of $Na^+$ was from 0 mM to 1.12 mM (from (a) to (i)), with $\lambda_{max}$ at 379.0 nm. Inset: curve-fitting analyses for the above complexation at 379.0 nm.

**Table 1**. Stability constants (log $K_S$) and Gibbs free energy changes ($-\Delta G$) for the complexation of alkali metal ions with chromogenic calix[4]arene derivatives **4**, **5** and **6** in $CH_3CN-H_2O$ (99:1/V:V) solution at 25°C

| Ligand | Cation | $K_S$ | log $K_S$ | $-\Delta G$ (kJ $mol^{-1}$) |
|---|---|---|---|---|
| **4** | $Na^+$ | 2230 | 3.35 | 19.11 |
| | $K^+$ | 380 | 2.58 | 14.74 |
| | $Rb^+$ | 190 | 2.28 | 13.01 |
| | $Cs^+$ | – | – | – |
| **5** | $Na^+$ | 2430 | 3.38 | 19.31 |
| | $K^+$ | 430 | 2.63 | 15.02 |
| | $Rb^+$ | 250 | 2.41 | 13.74 |
| | $Cs^+$ | – | – | – |
| **6** | $Na^+$ | 1940 | 3.29 | 18.76 |
| | $K^+$ | 400 | 2.60 | 14.86 |
| | $Rb^+$ | 190 | 2.30 | 13.10 |
| | $Cs^+$ | – | – | – |

The log $K_S$ values are the average of two or three independent runs: error <5% of the reported value. '–' represents the spectral changes are too small to allow the calculation of the stability constants.

excess $Na^+$ to the calix[4]arene derivatives solution, in the course of which two characteristic maximum absorption intensity at 280 and 379 nm gradually decreased, and a new peak at 480 nm intensified leading to one isobestic point at 408 nm. These results were interpreted as the result of formation of 1:1 complex, which was also further validated by a Job's curve (Fig. 2).

It is interesting to note that the changes in spectral patterns induced by $Na^+$ complexation with structurally similar calix[4]arene derivatives **4**-**6** are quite different from the complexation with other alkali ions, which suggests that $Na^+$ can be recognized, even visually, with the present chromogenic calix[4]arene. However, as shown in Figure 3, the complexation of other guest ions ($K^+$, $Rb^+$, $Cs^+$) exhibited only slight spectral changes under the experimental conditions.

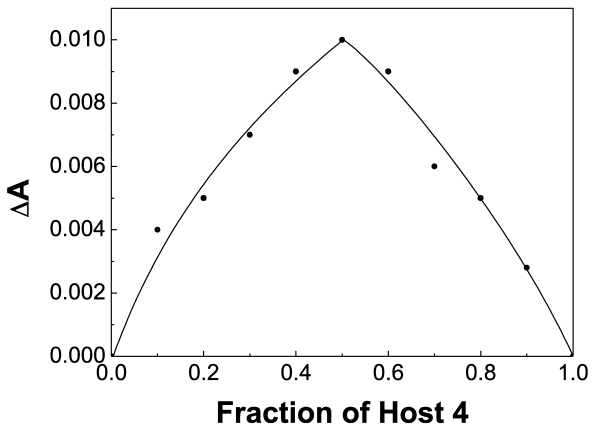


**Figure 2.** Continuous variation plot of **4** with sodium ion at 379.0 nm ([calix[4]arene derivative **4**]+[$Na^+$]=$3.0\times10^{-5}$ M).

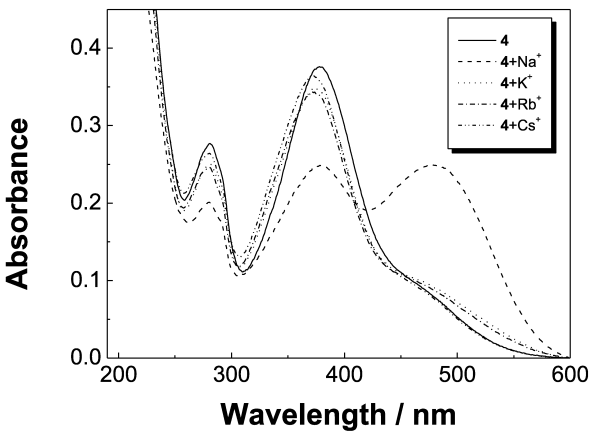


**Figure 3.** Absorption spectra of **4** in $CH_3CN-H_2O$=99:1 upon addition of alkali metal ions. [**4**]=$0.8\times10^{-5}$ M, [$Na^+$]=$1.12\times10^{-3}$ M, [$K^+$]=$1.02\times10^{-3}$ M, [$Rb^+$]=$1.00\times10^{-3}$ M, [$Cs^+$]=$1.05\times10^{-3}$ M.

## 2.2. Cation binding ability and selectivity

It is well known that the cation binding ability and selectivity upon complexation with calix[4]arene and its derivatives are influenced by many factors, such as the ion surface charge density, spatial arrangement of the donor atoms, size-fit relationship between cation and calix[4]-arene, as well as the cooperative binding of the appended side-arms, and so on.[16a] In this work, it is considered that the induced three-dimensional cavity of the parent calixarene platform and the attached side arms upon complexation play an important role in cation binding ability and selectivity. As can be seen from Table 1, compounds **4**-**6** show relatively strong binding ability to all of the metal ions examined, especially for sodium ion. It is well known that the diameters of metal cations examined (1.90–3.76 Å)[16b] are larger than that of the annuli of the parent calix[4]arene (ca. 1.00 Å).[1a] Therefore, the high complexes stability constants ($K_S$) and Gibbs free energy changes ($-\Delta G^\circ$) upon complexation of calix[4]arene derivatives **4**-**6** with cations may be caused by the attached side arms possessing the donor atoms to afford the enhancement binding sites. In order to visualize the cations binding properties of calix[4]arene derivatives **4**-**6**, the changing profile of $K_S$ is plotted as a function of ionic radius of alkali metal ions in Figure 4.

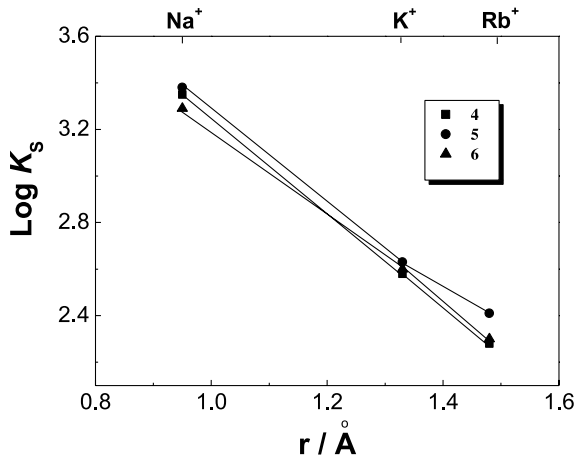


**Figure 4.** Complex stability constant ($K_S$) as a function of ionic radius ($r$, Å) for the complexation of alkali ions with **4**-**6** in acetonitrile–water (99:1) at 25°C.

As illustrated in Figure 4, all host compounds **4**-**6** display the different cation binding ability and gradually decreasing tendency in $K_S$ according to the sequence of ionic radius increase. This means that the size-fitting concept between host and guest seems to be the predominant factors that determine the complex stability and selectivity upon complexation with alkali metal ions. Meanwhile, compounds **4**-**6** give similar $K_S$ profiles, and nearly linear decrease with increasing ionic radius throughout the alkali metal series $Na^+-Rb^+$ (according to the sequence of ionic radius). Therefore, the higher selectivity of structure analogous ligands **4**-**6** for $Na^+/K^+$ is up to 5–7 times. As compared with calix[4]arene derivative **6**, compounds **4** and **5** possessing the electron withdrawing effect of nitro groups may be advantageous for the ionization of hydroxy groups resulting in stronger electrostatic interaction with metal ions, giving the slightly enhanced cation binding ability and selectivity. And then, the values of $K_S$ for complexation of $Na^+$ with compounds **4** and **5** are increased to 2230 and 2430 $M^{-1}$ from 1940 $M^{-1}$ for **6**, respectively. It is concluded therefore that the introducing functional side arms to the lower rim of calix[4]arene alter not only the binding ability for metal ions but also the relative cation selectivity significantly.

### 2.3. Chromogenic effect upon side arms binding

A great number of investigations indicated that functional side-arms attached to parent molecular receptors such as crown ethers,[17–23] cyclodextrins,[24–26] and calixarenes[16a,27–32] could bond cooperatively a guest molecule or an ion through induced 3D cavity. In the present case, a pair of characteristic double peaks at 3.3 and 4.1 ppm of the methylene protons in the $^1$H NMR and the double peaks at 30.07 and 30.15 ppm of the methylene carbon atoms bridging the aromatic rings in the $^{13}$C NMR spectrum of complex **4**–$Na^+$ indicated that calix[4]arene **4** still adopted a typical cone conformation upon complexation with the metal ion,[34,35] giving a molecular platform. Furthermore, the large Gibbs free energy changes ($-\Delta G^\circ$=13–19 kJ mol$^{-1}$) demonstrated that the azophenol side arm(s) may be involved in the binding of metal ions, leading to an induced 3D cavity between the lower portion of the platform and the azophenol side arm(s). The highest stability constants upon complexation of $Na^+$ with **4**-**6** indicated that the induced 3D cavities seem to be best fitted to the diameter of sodium ion in terms of size and spatial arrangement. The color changes of hosts **4**-**6** for complexation with sodium ion from yellow to red and significant large bathochromic shifts ($\lambda_{max}$ 379→480 nm) displayed the remarkable chromogenic effect upon side arms binding. One possible explanation for chromogenic effect is that the protonionizable chromogenic calixarene undergoes complete or partial deprotonation on the pendant azophenol groups to yield anions, which in turn interact intramolecularly with a metal ion.[33]

In order to extensively investigate the origin of color change, the pH-dependent liquid-liquid extraction experiments of **4** were performed at 25°C as shown in Figure 5. The solution color of resulting complex of **4** with $Na^+$ changes from yellow to red at pH=7. However, the solution color of **4** is colorless and the UV absorption peaks show a large blue shift from 376 to 352 nm in the presence or absence of $Na^+$ at pH=1, which is attributed to the protonation of the azophenol groups. In contrast to the observation from the acidic condition, the solution color of **4** is red in the presence or absence of $Na^+$ at pH=12. On the other hand, the absorption peak of complex of **4** with $Na^+$ at 483 nm at pH=7 is strongly enhanced and shifts from 483 to 497 nm in the basic condition. This seems reasonable since host **4** releases protons from the azophenol units to form phenolate in basic condition, which leads to the stronger electrostatic interaction between **4** and $Na^+$, accompanying with a stronger absorption at 497 nm. Unlike the case of $Na^+$, the resulting complexes of other alkali metal ions with **4** did not show any significant color changes, and therefore the calix[4]arenes possessing azophenols groups could be potentially used as chemosenor for $Na^+$.

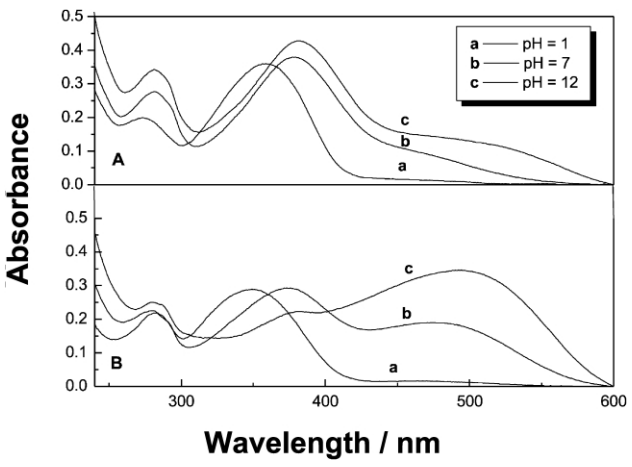


**Figure 5.** UV–Vis spectra of **4** ($8.0\times10^{-5}$ M) in the absence (A) and presence (B) of $Na^+$. The aqueous phase of pH=1 and 12 were adjusted by HCl and tetramethylammonium hydroxide, respectively.

From the results obtained above, we can conclude that introducing proper chromogenic side arms to the parent calixarene unit could not only enhance ionic binding ability but also respond selectively to specific ion.

## 3. Experimental

### 3.1. General

Melting points were measured by an XT-4 apparatus are uncorrected. $^1$H NMR spectra were recorded at 300 MHz in $CDCl_3$ solution on a Varian INVOA instrument, using tetramethylsilane as an internal reference. Infrared and ultraviolet spectra were recorded on Shimadzu Bio-Rad FTS 135 and Shimadzu UV-2401/PC instruments, respectively. Elemental analyses were performed on a Perkin–Elmer 2400C instrument. Mass spectra were measured by using a VG ZAB-HS instrument.

### 3.2. Materials

Starting materials were commercially available unless otherwise noted. 5,11,17,23-tetra-*tert*-butyl-25,27-bis(2-cyanomethoxy)-26,28-dihydroxycalix[4]arene (**2**) was synthesized by the reaction of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrahydroxy-calix[4]arene with chloroacetonitrile in the presence of potassium carbonate and sodium iodide in anhydrous acetone, according to the procedure reported by Collins et al.[13] Calix[4]arene derivative **3** was obtained by reducing **2** with $LiAlH_4$ in anhydrous THF.[14] The azosalicylaldehyde intermediates were prepared from substituted aniline (2.0 g), sodium nitrite (1.0 g), and conc. HCl (5.8 mL) in water (10 mL). This mixture was stirred for 0.5 h in an ice bath. Then, carbamide (0.15 g) was added to remove the unreacted sodium nitrite. Sodium hydroxide (1.6 g), salicylaldehyde (1.5 mL) in water (300 mL) were then slowly added to the above solution, which was stirred for another 2 h at 0°C. The precipitate was collected, dried and obtained orange powder, which was recrystallized with toluene to give pure products in the yields of 50–70%.[14b] The reagent grade chemicals NaCl, KCl, RbCl and CsCl were heated at 150°C for 3 days before use.

**3.2.1. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-[(2-hydroxy-5-(4-nitro-azo)benzyl idene)amino]ethoxy]-26,28-dihydroxycalix[4]arene (4).** The reaction of *p*-nitrylazosaliayl-aldehyde (0.74 g, 2.72 mmol) with 1,3-alternately substituted 25,27-bis(2-aminoethoxy)-26,28-calix[4]arene **3** (1.0 g, 1.36 mmol) in anhydrous THF (40 mL) was stirred for 4 h at 70°C under $N_2$. After cooling,

the precipitate obtained was filtered and recrystallized from anhydrous THF to give an orange powder of **4** (0.65 g, 39%), mp>300°C. $^1$H NMR ($CDCl_3$), $\delta$: 0.88 (s, 18H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$), 3.25 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.13 (t, 4H, $J$=5.2 Hz, $NCH_2$), 4.18 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.27 (t, 4H, $J$=5.2 Hz, $OCH_2$), 6.68 (s, 2H, ArH), 6.70 (s, 4H, ArH), 6.97 (d, 2H, $J$=9.0 Hz, ArH), 7.0 (s, 4H, ArH), 7.90–7.98 (m, 6H, ArH), 8.34–8.38 (m, 4H, ArH and NCH), 8.70 (s, 2H, ArOH); $^{13}$C NMR (75 Hz, $CDCl_3$) $\delta$: 31.6, 33.8, 57.5, 74.6, 118.0, 119.0, 122.9, 124.7, 125.0, 125.7, 127.3, 127.6, 129.6, 132.0, 141.7, 144.6, 147.3, 148.1, 149.4, 150.2, 155.9, 167.1, 167.4. Anal. calcd for $C_{74}H_{80}N_8O_{10}$: C, 71.59; H, 6.49; N, 9.03; found: C, 71.66, H, 6.48, N, 9.02. FT-IR $\nu$ (KBr)/cm$^{-1}$ 3524, 2958, 2902, 2867, 1641, 1617, 1484, 1338, 1105, 855. FAB-MS $m/z$: 1241.6 ($M^+$). UV/Vis ($CH_3CN$) $\lambda_{max}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 379 (5037), 281.5 (3668).

**3.2.2. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-[(2-hydroxy-5-(2-nitro-azo)benzyl idene)amino]ethoxy]-26,28-dihydroxycalix[4]arene (5).** Double-arm calix[4]-arene **5** was prepared in yield 68% according to a similar procedure described above, mp>300°C. $^1$H NMR ($CDCl_3$), $\delta$: 0.88 (s, 18H, $C(CH_3)_3$), 1.26 (s, 18H, $C(CH_3)_3$), 3.25 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.16 (t, 4H, $J$=5.2 Hz, $NCH_2$), 4.20 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.27 (t, 4H, $J$=5.2 Hz, $OCH_2$), 6.69 (s, 2H, ArH), 6.76 (s, 4H, ArH), 6.95–7.04 (m, 6H, ArH), 7.48–7.51 (m, 2H, ArH), 7.59 (s, 4H, ArH), 7.88–7.94 (m, 4H, ArH and NCH), 8.67 (s, 2H, ArOH); $^{13}$C NMR (75 Hz, $CDCl_3$) $\delta$: 31.6, 33.8, 57.9, 74.7, 118.1, 118.7, 124.0, 125.0, 125.6, 127.6, 128.1, 128.8, 129.6, 132.2, 132.9, 141.4, 144.7, 147.1, 149.5, 150.3, 166.9, 167.5. Anal. calcd for $C_{74}H_{80}N_8O_{10}$: C, 71.59; H, 6.49; N, 9.03. Found: C, 71.39, H, 6.40, N, 8.88. FT-IR $\nu$ (KBr)/cm$^{-1}$ 3523, 2960, 2902, 2873, 1639, 1617, 1527, 1484, 1113, 873. FAB-MS $m/z$: 1241.6 ($M^+$). UV/Vis ($CH_3CN$) $\lambda_{max}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 362 (4176), 277 (3743).

**3.2.3. Synthesis of 5,11,17,23-tetra-*tert*-butyl-25,27-bis[2-[(2-hydroxy-5-(4-chloro-azo)benzyl-idene)amino]-ethoxy]-26,28-dihydroxycalix[4]arene (6).** Double-arm calix[4]arene **6** was prepared in yield 78% according to a similar procedure described above, mp>300°C. $^1$H NMR ($CDCl_3$), $\delta$: 0.90 (s, 18H, $C(CH_3)_3$), 1.27 (s, 18H, $C(CH_3)_3$), 3.24 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.18 (t, 4H, $J$=5.2 Hz, $NCH_2$), 4.22 (d, 4H, $J$=12 Hz, $ArCH_2Ar$), 4.27 (t, 4H, $J$=5.2 Hz, $OCH_2$), 6.71 (s, 4H, ArH), 6.79 (s, 2H, ArH), 6.95–6.99 (m, 6H, ArH), 7.45– 7.48 (m, 4H, ArH), 7.79–7.93 (m, 6H, ArH and NCH), 8.67 (s, 2H, ArOH); $^{13}$C NMR (75 Hz, $CDCl_3$) $\delta$: 31.7, 33.8, 58.1, 74.7, 118.3, 123.7, 125.0, 125.6, 127.1, 127.6, 128.0, 129.3, 132.2, 136.1, 141.5, 144.8, 147.2, 149.6, 150.4, 151.0, 165.2, 167.6. Anal. calcd for $C_{74}H_{80}N_6O_6Cl_2$: C, 72.83; H, 6.61; N, 6.89. Found: C, 72.95, H, 6.60, N, 7.00. FT-IR $\nu$ (KBr)/cm$^{-1}$ 3526, 2959, 2903, 2869, 1638, 1484, 1114, 834. FAB-MS $m/z$: 1220.3 ($M^+$). UV/Vis ($CH_3CN$) $\lambda_{max}$/nm ($\varepsilon$/M$^{-1}$ cm$^{-1}$) 356.5 (7528), 277.5 (6869).

### 3.3. Spectral measurements

Differential absorption spectra were obtained directly using the instrument according to its normal procedures. The quartz cells (1 cm) were kept at constant temperature (25.0±0.1°C) with circulating water from a constant-temperature water bath.

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