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BODIPY appended *cone*-calix[4]arene: selective fluorescence changes upon Ca^{2+} binding

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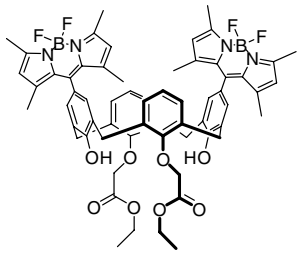
Abstract—BODIPY appended new calix[4]arene diethyl ester (**1**) has been synthesized in the cone conformation. With respect to fluorescence intensity changes upon metal ion complexation, **1** shows a Ca^{2+} ion selectivity over other metal cations. Presence of two proximal hydroxyl groups and two facing ethyl esters in BODIPY-calix[4]arene were observed to play an important role in exhibiting its selective Ca^{2+} ion binding.

The investigation of specific chemosensors for the efficient detection of metal ion analytes is one of the most important areas in supramolecular chemistry because of their toxic impacts on our environments, roles in living systems, and chemical significances.[1] The fluorophore (signaling moiety) makes human–molecule communication possible through a light signal resulting from its changes in photophysical characteristics, whereas the recognition unit (ionophore) linked to the fluorophore is responsible for the selectivity and cation binding efficiency of the entire chemosensor.[2,3] To develop this fluorescence chemosensor, we have focused on the boron dipyrromethene (BODIPY) fluorophore. Among fluorophores, BODIPY is well known for fluorescent dyes with high quantum yields, large extinction coefficients, and narrow emission bands.[4] These properties facilitated their application in many fields, such as fluorescent labeling of biomolecules, ion sensing and signaling, energy transfer cassettes, light harvesting systems and fluorescent stains.[5–9]

Calix[4]arenes are important macrocyclic compounds and also ideal platforms for the development of complexing agents for metal ions. Calixarenes functionalized with appropriate cation-ligating groups, such as carboxylic acid, ester, amide, crown ether, and azacrown ether groups, are good candidates for cation recognition due to their high selectivity toward specific cations.[10] Reported calixarene-based fluorescence sensors utilize photo-physical changes produced by a cation binding: photo-induced electron transfer (PET),[11] excimer/exciplex formation and extinction,[12] or energy transfer.[13]



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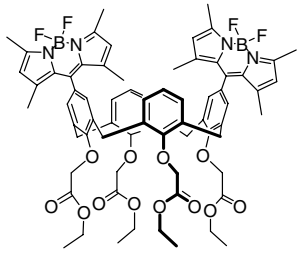

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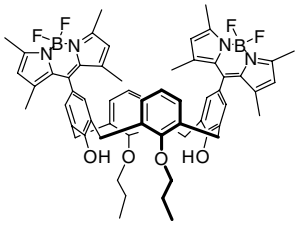

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Keywords: Calixarenes; Fluorescence; Reverse PET.
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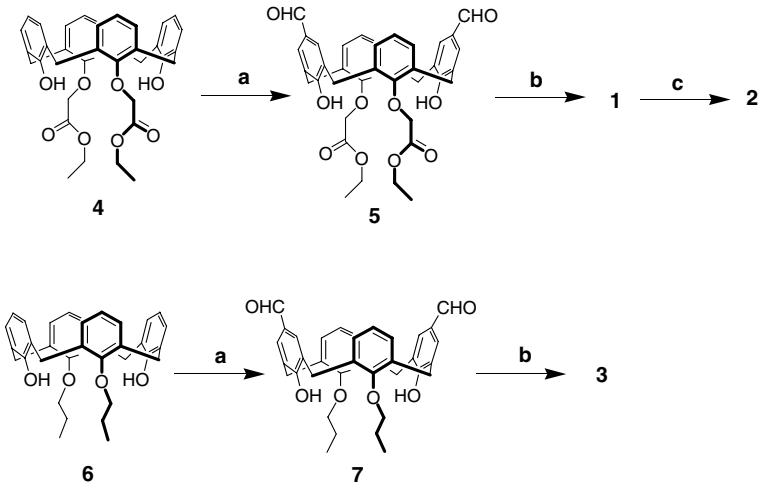

Scheme 1. Synthetic route to fluoroionophores **1**–**3**. Reagents: (a) $SnCl_4/CHCl_2OCH_3/CHCl_3$; (b) 2,4-dimethylpyrrole/TFA/*p*-chloranil/Et_3N/$BF_3{\cdot}Et_2O/CH_2Cl_2$ and (c) ethyl bromoacetate/K_2CO_3/acetone.

In this letter, we report on a synthesis of BODIPY appended calix[4]arene chemosensor exhibiting a unique fluorescent response to the Ca^{2+} ion. In addition, to prove the causative factors for this response, its analogs **2** and **3** were also prepared as references.

Syntheses of molecules **1**–**3** are depicted in Scheme 1.[14] **4**[15] and **6**[16] were prepared by adaptation of reported procedures elsewhere. Compounds **5** and **7** were synthesized in 57% and 34% yield, respectively, by the selective formylation of **4** and **6** using $SnCl_4$ and $CHCl_2OCH_3$ in $CHCl_3$. Compounds **5** and **7** were treated with 2,4-dimethylpyrrole in the presence of TFA, which were subsequently oxidized by *p*-chloranil, neutralized with Et_3N, and treated with $BF_3{\cdot}Et_2O$ to produce the desired BODIPY derivatives **1** and **3**, respectively. Reaction of **1** with ethyl bromoacetate in the presence of 1.0 equiv of K_2CO_3 in acetone gave **2** in 72% yield.[14]

Metal ion binding properties of **1**–**3** were investigated by monitoring fluorescence and UV/vis changes upon the addition of Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions. **1** shows a sharp and strong absorption band at 495 nm (Fig. 1). Upon the addition of 100 equiv of each metal ion, no distinctive change of **1** was observed. Compounds **2** and **3** show the same UV/vis spectral changes as **1** does.

To gain insight into the fluorescence change of **1** upon metal ion complexation, emission spectra of **1** for various metal cations used in UV/vis measurement were taken and are represented in Figure 2. Free **1** shows an intense greenish-yellow fluorescence and emits the florescence at 506 nm in CH_3CN solution ($\lambda_{ex} =$ 485 nm). Fluorescence intensity of **1** selectively diminished as a function of $[Ca^{2+}]$ (Fig. 3) compared to other metal cations, whereas those of **2** and **3** show relatively low selectivity toward all metal cations tested. According to the extent of the fluorescence emission changes, we could obtain the association constants[17] of **1** ($K_a = 5.2 \times 10^7\ M^{-1}$) for Ca^{2+} ion.

The quenching phenomenon of **1** upon Ca^{2+} ion binding is attributable to the reverse-PET (photo-induced electron transfer) mechanism.[18] When the Ca^{2+} ion strongly interacts with the lone pair electrons of the carbonyl oxygen atoms ($Ca^{2+}\cdots O{=}C$) with the aid of two proximal OHs,[19] then electron transfer occurs from BODIPY unit behaving as a PET donor to electron deficient carbonyl group as shown in Figure 4.

For complexation ratio between ligand and Ca^{2+} ion, we carried out Job's plot experiment by varying the concentrations of both **1** and Ca^{2+} ion (see Fig. 5). The maximum point at the mole fraction of 0.5 indicates that a typical 1:1 (ligand:metal) complexation performs in this case.

To elucidate a role of two proximal OHs and ester group in **1** for selective Ca^{2+} ion binding, tetraethyl ester derivative **2** was prepared. The emission of **2** by excitation at 485 nm is slightly quenched by either Ca^{2+} or

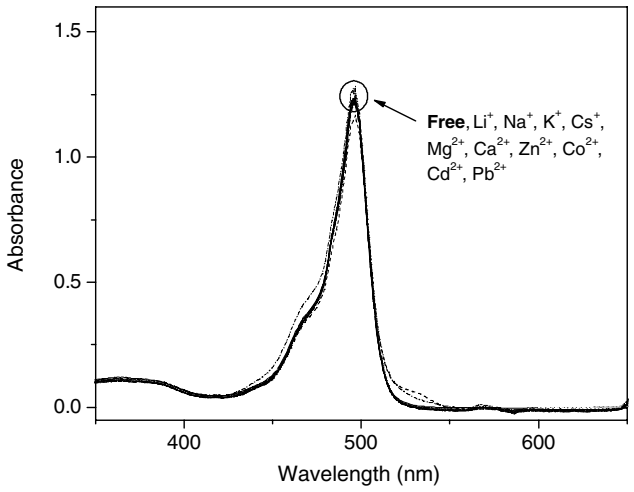

Figure 1. UV/vis spectra of **1** in the presence of 100 equiv of Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions. [**1**] = 20 μM in CH_3CN.

Na^+ ion binding because the cations are bound to the four ester groups.[20] As shown in Figure 6, addition of Na^+ or Ca^{2+} ion to a solution of **2** decreases the fluorescence intensity. For Ca^{2+} ion case, **1** is about two times more effective to quench the emission than is **2**. The association constant of **2** with Ca^{2+} ion is $4.34 \times 10^4\ M^{-1}$, which is smaller than that of **1** (vide supra), implicating that not only two carbonyl esters, but the two OH groups seem to take part in the Ca^{2+} complexation.

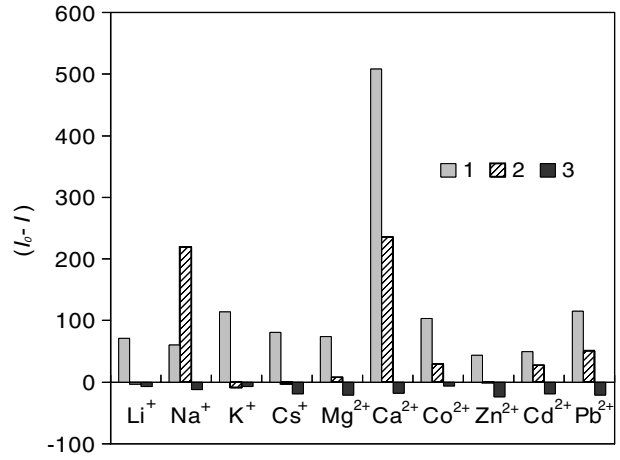

Figure 2. Reverse-PET: fluorescence emission changes $(I_0 - I)$ of 1.0 μM solutions of **1**–**3** in CH_3CN upon addition of 500 equiv of various metal ions. Excitation at 485 nm; I_0: fluorescence emission intensity of free **1**–**3**. I: fluorescence emission intensity of metal complexes of **1**–**3**. (+) and (−) denote fluorescence decrease and increase, respectively.

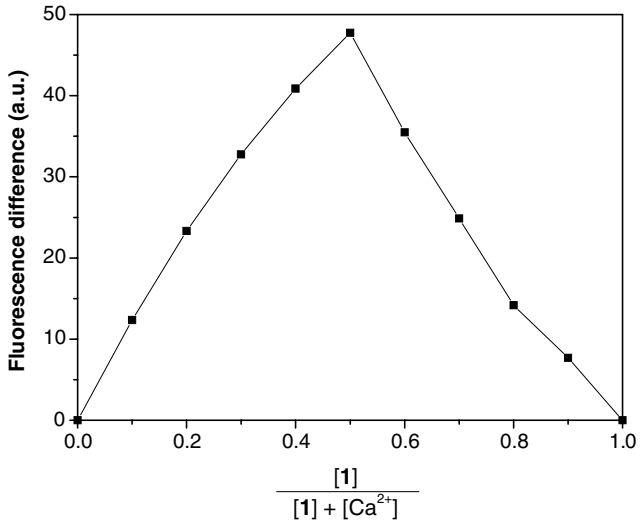

Figure 5. Job's plot for **1** Ca^{2+}. Y axis is for fluorescence changes of **1**.

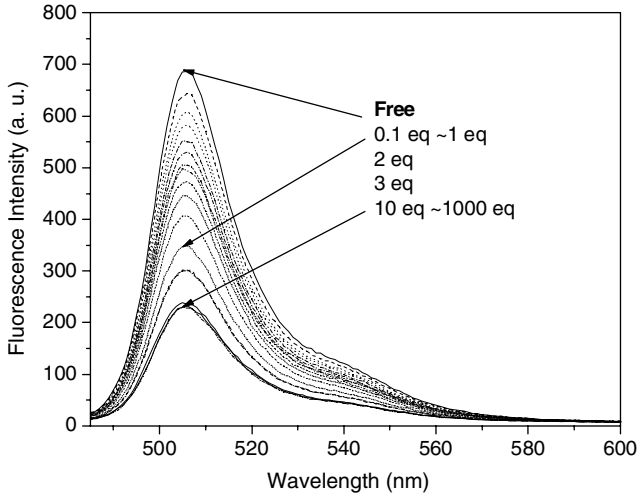

Figure 3. Fluorescence emission spectra of **1** (1.0 μM) for Ca^{2+} ion titration in CH_3CN ($\lambda_{ex} = 485$ nm).

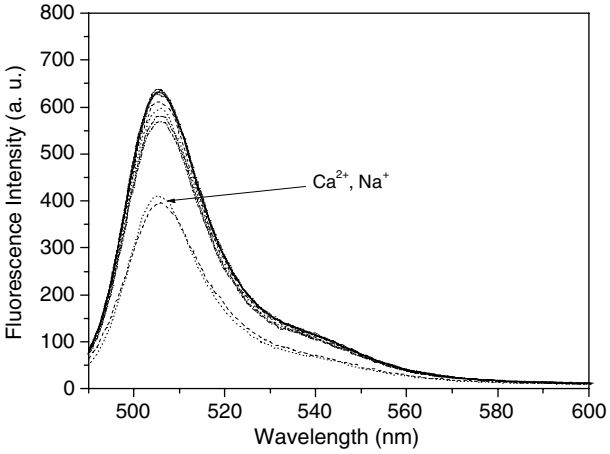

Figure 6. Fluorescence emission spectra of **2** (1.0 μM) in the presence of 500 equiv of Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Zn^{2+}, Co^{2+}, Cd^{2+}, and Pb^{2+} ions.

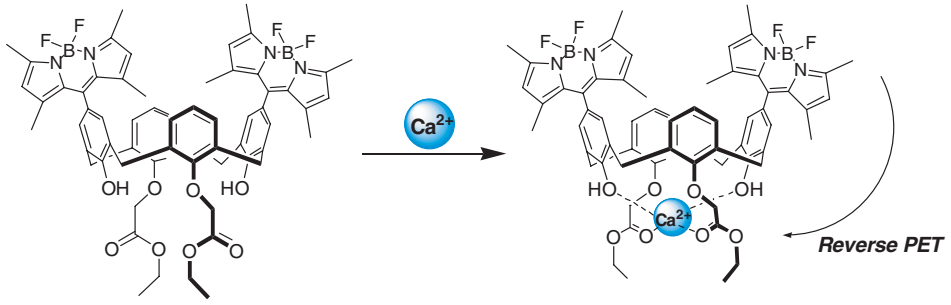

Figure 4. Plausible complexation mechanism of **1** with Ca^{2+} ion.

Compound **3** as the other reference without ester functional groups on the calix[4]arene lower rim was tested for the quenching behavior in Ca^{2+} ion binding. We, however, rarely observed fluorescence changes toward all metal ions tested including Ca^{2+} ion. This can be also a solid evidence for that the ester functional groups of the BODIPY calix[4]arene play a critical role in the complexation of the metal cations.

In conclusion, the *cone*-conformation calix[4]arene **1** exhibits a remarkable selectivity toward Ca^{2+} ion that suggests possible applications as a new fluorogenic ionophore for a sensing material useful for the Ca^{2+} ion. And the carbonyl oxygen atoms of the two ester groups and two hydroxyl groups take part in the calcium ion complexation, these two functional groups play an important role in the Ca^{2+} ion selectivity in chemosensors.

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14. *General*: Uncorrected melting points (Mps), Buchi 500. ^{1}H NMR and ^{13}C NMR, Varian 200 MHz (δ in ppm from TMS, *J* in Hertz). FAB MS mass spectra, JEOL-JMS-HX 110A/110A High Resolution Tendem Mass Spectrometry in Seoul National University (Korea). All the reactions were run under a nitrogen atmosphere. SiO_2 (Geduran 1.11567) was used for column chromatography. All reagents and solvents were commercial and used without further purification. Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions of **1**–**3** (1.0 μM) were prepared in CH_3CN. For all measurements, excitation was at 485 nm with excitation and emission slit widths at 1.5 nm. Fluorescence titration experiments were performed using 1.0 μM solutions of **1**–**3** in CH_3CN and various concentrations of metal perchlorate in CH_3CN.

Job plot experiment. Stock solutions of **1** (1.0 μM) in MeCN and $Ca(ClO_4)_2$ (1.0 μM) in MeCN were prepared. The concentrations of each MeCN solution were varied, but the total volume was fixed to be 4.0 mL.

Preparation of 25,27-bis(ethoxycarbonylmethoxy)-5,17-bis(BODIPY)calix[4]arene, cone (**1**). To a solution of 2,4-dimethylpyrrole (0.169 g, 0.97 mmol) and **5** (250 mg, 0.38 mmol) in dried CH_2Cl_2, two drops of CF_3CO_2H was added. The yellow solution was stirred for 3 h at room temperature under N_2. A solution of *p*-chloranil (0.79 g, 0.97 mmol) in CH_2Cl_2 (100 mL) was then added. After stirring for 30 min, Et_3N (15 mL) and $BF_3{\cdot}OEt_2$ (15 mL) were subsequently added until a bright-green fluorescence was observed. The solution was washed with water, and the organic layer was dried over anhydrous $MgSO_4$. Removal of the organic solvent in vacuo afforded a reddish solid. Column chromatography on silica gel with EtOAc–hexane (1:2) as eluents gave 0.89 g (42%) of **1**. Mp: 176–180 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.26 (s, 2H, $Ar'_{calix}-OH$), 6.99 (s, 4H, $Ar'_{calix}-H_m$), 6.86 (d, 4H, Ar_{calix}–H_m, $J = 7.79$ Hz), 6.71–6.62 (t, 2H, Ar_{calix}–H_p, $J = 7.26$ Hz), 4.70 (s, 4H, $Ar_{calix}OCH_2CO$),4.55 (d, 4H, $Ar'CH_2Ar$, $J = 12.8$ Hz), 4.39–4.53 (q, 4H, Ar_{calix}–OCH_2CH_3), 3.44 (d, 4H, $Ar'CH_2Ar$, $J = 13.2$ Hz), 1.54 (s, 6H, pyrrole–CH_3), 1.43–1.32 (t, 6H, $Ar_{calix}OCH_2CH_3$, $J = 7.28$ Hz), 1.25 (s, 6H, pyrrole–CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): 176.0, 173.9, 168.8, 153.0, 152.2, 150.9, 147.6, 133.2, 132.9, 128.7, 128.4, 127.9, 120.8, 119.0, 112.4, 88.6, 72.4, 61.9, 61.3, 52.1, 31.4, 29.6, 14.1 ppm; FAB MS *m*/*z* (M^+): calcd, 1088.79. Found, 1088.70. Anal. Calcd for $C_{62}H_{62}B_2F_4N_4O_8$: C, 68.39; H, 5.74. Found:C, 68.36; H, 5.72.

Preparation of 25,26,27,28-tetrakis(ethoxycarbonylmethoxy)-5,17-bis(BODIPY)calix[4]arene, cone (**2**). A solution of **1** (0.1 g, 0.092 mmol), ethyl bromoacetate (0.184 mmol, 0.018 mL), and anhydrous K_2CO_3 (0.084 mg, 0.092 mmol) in dried acetone was refluxed for 12 h. After the organic solvent was removed in vacuo, the residue was dissolved in CH_2Cl_2 and washed three times with water. The organic layer was dried over anhydrous $MgSO_4$ and evaporated in vacuo to yield 80 mg (72%) of **2** as a solid. Mp: 163–165 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 7.57 (s, 2H, ArH_m), 7.36 (s, 2H, ArH_m), 6.66 (s, 4H, $Ar'H_m$), 6.33 (d, 2H, $Ar'H_p$), 5.41 (s, 4H, pyrrole–*H*), 5.25 (d, 4H, $Ar'CH_2Ar$, $J = 13.0$ Hz), 4.91 (s, 4H, $Ar'OCH_2CO$), 4.82 (s, 4H, $ArOCH_2CO$), 4.64 (m, 8H, OCH_2CH_3, $J = 13.2$ Hz), 3.62 (d, 4H, $Ar'CH_2Ar$, $J = 13.2$ Hz), 2.87 (br s, 12H, OCH_2CH_3, $J = 7.00$ Hz), 1.65 (br s, 24H, pyrrole–CH_3, $J = 3.39$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): 170.6, 169.7, 167.7, 157.6, 155.9, 155.5, 155.1, 149.3, 143.8, 143.0, 142.2, 137.8, 132.9, 131.8, 129.7, 128.9, 128.8, 128.0, 123.1, 121.5, 121.3, 72.5, 71.5, 69.9, 62.0, 61.2, 60.8, 32.0, 30.0, 15.3, 14.9, 14.5 ppm; FAB MS *m*/*z* (M^+): calcd, 1260.97. Found, 1260.00. Anal. Calcd for $C_{70}H_{74}B_2F_4N_4O_{12}$:C, 66.67; H, 5.92. Found: C, 66.71; H, 5.95.

Preparation of 25,27-dipropyloxy-5,17-bis(BODIPY)calix[4]arene, cone (**3**). Compound **3** was prepared by modification of the procedure given above for **1**. Column chromatography on silica gel with EtOAc–hexane (1:3) as

eluents gave 50 mg (14%) of **3**. Mp: 185–190 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 8.47 (s, 2H, $Ar'_{calix}-OH$), 6.99 (s, 4H, $Ar'_{calix}-H_m$), 6.85 (d, 4H, Ar_{calix}–H_m, $J=7.20$ Hz), 6.69–6.65 (t, 2H, Ar_{calix}–H_p, $J=6.99$ Hz), 6.00 (s, 2H, pyrrole–*H*), 5.89 (s, 2H, pyrrole–*H*), 4.39 (d, 4H, $Ar'CH_2Ar$, $J=12.7$ Hz), 4.01 (t, 4H, $Ar_{calix}OCH_2$-CH_2CH_3), 3.41 (d, 4H, $Ar'CH_2Ar$, $J=12.5$ Hz), 2.56 (d, 12H, pyrrole–CH_3), 2.15 (q, 4H, $Ar_{calix}OCH_2CH_2CH_3$), 1.58 (d, 12H, pyrrole-CH_3), 1.41–1.32 (t, 6H, Ar_{calix}–$OCH_2CH_2CH_3$, $J=7.13$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): 190.9, 160.2, 159.6, 151.6, 134.9, 132.3, 131.5, 130.9, 129.8, 129.3, 128.9, 128.5, 128.4, 126.5, 125.6, 78.5, 31.2, 28.7, 23.4, 23.2, 10.8, 10.5 ppm; FAB MS *m*/*z* (M^+): calcd, 1000.77. Found, 1000.54. Anal. Calcd for $C_{60}H_{62}B_2F_4N_4O_4$: C, 72.31; H, 6.24. Found:C, 72.35; H, 6.21.

Preparation of 25,27-bis(ethoxycarbonylmethoxy)-5,17-diformylcalix[4]arene, cone (**5**). A solution of **4** (500 mg, 0.83 mmol) in $CHCl_3$ (200 mL) was treated with α,α′-dichloromethyl methyl ether (0.2 mL, 2.1 mmol). The reaction mixture was stirred for 10 min at room temperature, and then $SnCl_4$ (1.0 mL, 8.3 mmol) was added dropwise. The reaction mixture was stirred for an additional 3 h at room temperature, treated with water (300 mL), and extracted with CH_2Cl_2 (300 mL). The organic layer was washed three times with water, dried over anhydrous $MgSO_4$, and evaporated in vacuo to afford an oily residue. Column chromatography on silica gel with EtOAc–hexane (1:3) as eluents gave 0.39 g (71%) of **5**. Mp: 174–176 °C; IR (KBr pellet, cm^{-1}): 3374, 2994, 1759, 1683; ^{1}H NMR (200 MHz, $CDCl_3$) δ: 9.78 (s, 2H, $Ar'_{calix}-CHO$), 8.69 (s, 2H, Ar_{calix}–*OH*), 7.62 (s, 4H, $Ar'_{calix}-H_m$), 6.99 (d, 4H, Ar_{calix}–H_m, $J=7.99$ Hz), 6.84–6.80 (t, 2H, Ar_{calix}–H_p, $J=6.59$ Hz), 4.73 (s, 4H, $Ar_{calix}OCH_2CO$), 4.50 (d, 4H, $Ar'CH_2Ar$, $J=13.2$ Hz), 4.41–4.30 (q, 4H, OCH_2CH_3), 3.54 (d, 4H, $Ar'CH_2Ar$, $J=13.2$ Hz), 1.39–1.31 (t, 6H, OCH_2CH_3, $J=7.20$ Hz); ^{13}C NMR (50 MHz, $CDCl_3$): 190.8, 168.6, 159.2, 152.0, 132.2, 130.9, 129.5, 128.5, 128.4, 126.0, 72.3, 61.6, 31.2, 14.1 ppm; FAB MS *m*/*z* (M^+): calcd, 652.69. Found, 652. 86. Anal. Calcd for $C_{38}H_{36}O_{10}$: C, 69.93; H, 5.56. Found: C, 69.94; H, 5.56.

Preparation of 25,27-dipropyloxy-5,17-diformylcalix[4]-arene, cone (**7**). Compound **7** was prepared by modification of the procedure given above for **5**. Column chromatography on silica gel with EtOAc–hexane (1:3) as eluents gave 80 mg (36%) of **7** as a white solid. Mp: 184–188 °C; IR (KBr pellet, cm^{-1}): 3138, 2973, 1673; ^{1}H NMR (50 MHz, $CDCl_3$) δ: 9.79 (s, 2H, $Ar'_{calix}-CHO$), 8.74 (s, 2H, Ar_{calix}–*OH*), 7.63 (s,4H,$Ar'_{calix}-H_m$), 7.00 (d, 4H, Ar_{calix}–H_m, $J=7.85$ Hz), 6.86–6.81 (t, 2H, Ar_{calix}–H_p, $J=6.86$ Hz), 4.74 (s, 4H, $Ar_{calix}OCH_2CH_2CH_3$), 4.43 (d, 4H, $Ar'CH_2Ar$, $J=13.0$ Hz), 4.39–4.31 (q, 4H, Ar_{calix}–$OCH_2CH_2CH_3$), 3.55 (d, 4H, $Ar'CH_2Ar$, $J=13.2$ Hz), 1.41–1.32 (t, 6H, $Ar_{calix}OCH_2CH_2CH_3$, $J=7.19$ Hz); ^{13}C NMR (200 MHz, $CDCl_3$): 190.9, 160.2, 159.6, 151.6, 134.9, 132.3, 131.5, 130.9, 129.8, 129.3, 128.9, 128.5, 128.4, 126.5, 125.6, 78.5, 31.2, 28.7, 23.4, 10.8, 10.5 ppm; FAB MS *m*/*z* (M^+): calcd, 564.67. Found, 565. 20. Anal. Calcd for $C_{36}H_{36}O_6$: C, 76.57; H, 6.43. Found: C, 76.54; H, 6.46.

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