

An Excimer-Based, Binuclear, On–Off Switchable Calix[4]crown Chemosensor

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Abstract: A new fluorescent chemosensor with two different types of cation binding sites on the lower rims of a 1,3-alternate calix[4]arene (**1**) is synthesized. Two pyrene moieties linked to a cation recognition unit composed of two amide groups form a strong excimer in solution. For **1**, the excimer fluorescence is quenched by Pb²⁺, but revived by addition of K⁺ to the Pb²⁺ ligand complex. Thus, metal ion exchange produces an on–off switchable, fluorescent chemosensor. Computational results show that the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbitals (LUMO) of the two pyrene moieties interact under UV irradiation of **1** and its K⁺ complex, while such HOMO–LUMO interactions are absent in the Pb²⁺ complex.

Introduction

Fluorescent chemosensors capable of selectively recognizing cations have potential analytical applications in many different fields, including chemistry, biology, and medicine.^{1–4} Most of the fluorescent chemosensors for cations are composed of a cation recognition unit (ionophore) together with a fluorogenic unit (fluorophore) and are called fluoroionophores.³ An effective fluorescence chemosensor must convert the event of cation recognition by the ionophore into an easily monitored and highly sensitive light signal from the fluorophore.⁵ As fluorogenic units, pyrenes (Py) are one of the most useful because of their relatively efficient excimer formation and emission.⁶ Since the intensity ratio of the excimer to the monomer emission (I_E/I_M) is sensitive to conformational changes of the pyrene-appended receptors, changes in I_E/I_M upon metal ion complexation can be an informative parameter in various sensing systems.^{1,7,8} For

the formation of an excimer of pyrenes, Broan reported that a calixarene containing pyrenyl esters forms a strong intramolecular excimer because of a strong π – π interaction between two pyrenes.⁹ In addition, Jin described a fluorescent calix[4]-arene with four ester groups, two of which are linked to pyrene units.¹⁰ The binding of Na⁺ to the carbonyl oxygen atoms of this compound causes its excimer emission to decrease while the monomer emission increases. Recently, it was reported that several fluoroionophores, with a crown ether unit and a pyrenyl moiety connected by a $-(CH_2)_n-$ spacer, show moderate Na⁺ and K⁺ selectivities based on 1:1 complex formation in nonaqueous solution.¹¹ Even more interestingly, one of them was found to exhibit a supramolecular function in the presence of γ -cyclodextrin (γ -CD) to provide a remarkably high sensitivity and selectivity for K⁺ in water.¹² From the various fluorescence studies of pyrene moieties, it is well-established that the monomer bands appear at 370–430 nm with well-resolved vibronic features and a broad featureless emission band peak occurs at approximately 480 nm.⁷ Also, pyrene excimer fluorescence has been established as a useful spectroscopic tool to probe intra- and intermolecular interactions of exchangeable apolipoproteins upon binding to lipids.¹³

Host molecules with more than one pyrenyl group exhibit intramolecular excimer emission by two different mechanisms. One results from π – π stacking of the pyrene rings in the free

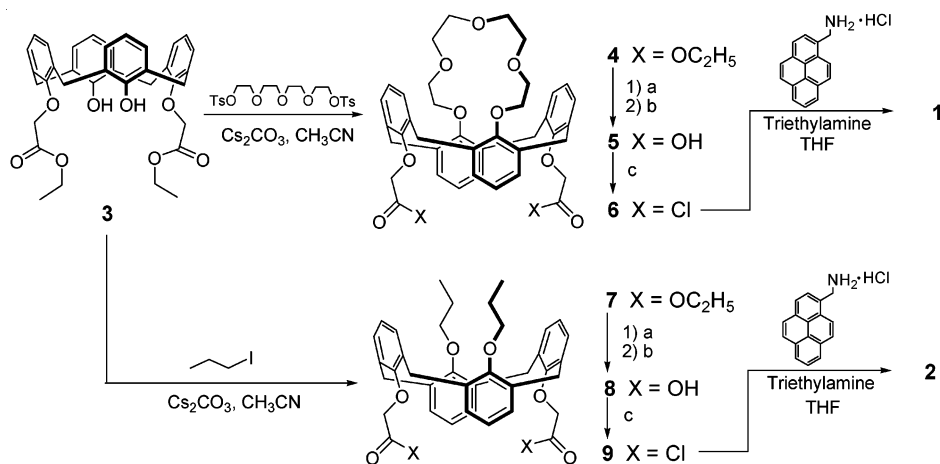
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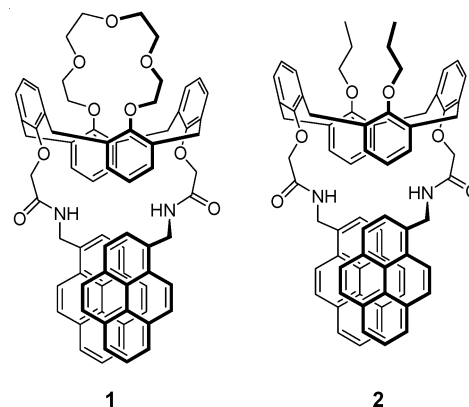
Scheme 1. Synthetic Routes to Fluorescent Chemosensors **1** and **2**^a

^a Conditions: (a) THF/H₂O/EtOH/NaOH; (b) HCl; (c) SOCl₂, toluene.

state, which results in a characteristic decrease of the excimer emission intensity and a concomitant increase of monomer emission intensity. The other mechanism is due to interaction of an excited pyrene (Py*) with a ground-state pyrene (Py). Some pyrene-containing hosts exhibit excimer emission due to the former mechanism¹⁴ and some due to the latter mechanism.¹⁵

Calixarenes with appropriate appended groups are good candidates as recognition moieties for cation probes because of their high selectivity toward specific cations.^{10,16–20} A 1,3-alternate calix[4]crown platform provides a crown ether ring for metal ion complexation with the potential for additional binding by cation– π interactions between the two rotated benzene rings and a polyether-complexed metal ion.¹⁵ Reported calixarene-based fluorescence sensors utilize photophysical changes produced by cation binding: photoinduced electron transfer (PET);^{18–21} photoinduced charge transfer (PCT);¹⁶ excimer/exciple formation and extinction;^{10,22} or energy transfer.²³ For the PET type, we have previously reported a series of “Molecular Taekwondo I and II” sensors with intramolecular metal ion exchange.²⁴ In these cases, the metal ion exchange processes are ascribed not only to repulsion between metal ions, but also to an allosteric effect. An allosteric effect results when the first binding event influences other binding or catalytic sites by some conformational changes, inhibiting or promoting the binding of other species.²⁵

Recently, the nature of electronic transitions that were analyzed from calculations by the collective electronic oscillator method was adapted to explain the fluorescence changes of a fluoride-selective sensor.²⁶ In addition, electron–hole interactions under UV irradiation were found to be consistent with an electron-transfer mode between the highest molecular orbital (HOMO) and three lowest unoccupied molecular orbitals (LUMOs). It seems reasonable to expect stabilization of the excited molecule when there is an attractive interaction between two regions with accumulated electron densities for the HOMO and LUMOs. Herein, we describe an “on–off” switchable calixcrown molecule that exhibits a change in excimer emission upon metal ion complexation, and we rationalize the function of this chemosensor on the basis of ab initio calculations.



Results and Discussion

Pyrene-appended, 1,3-alternate calix[4]arenes **1** and **2** were prepared by the synthetic routes depicted in Scheme 1. Calix[4]arene diethyl ester **3** in the cone conformation was synthesized by reaction of calix[4]arene with ethyl bromoacetate and 1 equiv of K₂CO₃ in MeCN.²⁷

Cyclization with tetraethyleneglycol ditosylate and alkylation with 1-iodopropane and Cs₂CO₃ in MeCN provided **4** and **7**, respectively, in the 1,3-alternate conformation in quantitative

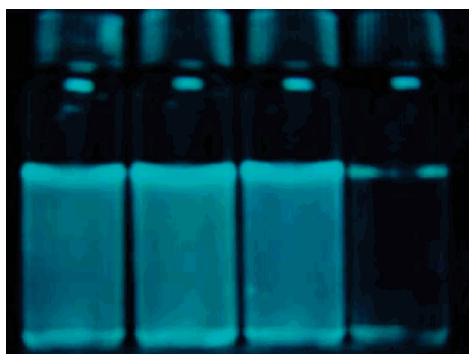
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Table 1. Fluorescence Changes ($I - I_0$) for **1** and **2** upon Addition of Various Metal Ions^a

ligand	λ_{em} (nm)	fluorescence changes ($I - I_0$)									
		Li ⁺	Na ⁺	K ⁺	Rb ⁺	Cs ⁺	Ag ⁺	Ca ²⁺	Mg ²⁺	Zn ²⁺	Pb ²⁺
1	375	-12.9	-10.4	-21.0	-23.8	-27.4	-27.9	59.8	-23.3	-7.3	-78.8
	470	1.9	-12.2	12.0	-3.5	7.2	-54.8	-46.2	4.2	-9.2	-381.4
2	375	-1.8	17.2	24.1	-2.2	-0.2	-90.5	-6.8	-22.4	-111.3	-170.9
	470	1.7	-29.6	-3.0	-3.4	16.3	-104.8	-15.5	-0.4	-79.4	-320.7

^a Conditions: **1** and **2**, 6 μ M in MeCN, excitation at 344 nm; metal ions, 500 equiv in acetonitrile. I_0 : fluorescence emission intensity of uncomplexed **1** and **2**; I : fluorescence emission intensity of metal ion-complexed **1** and **2**.



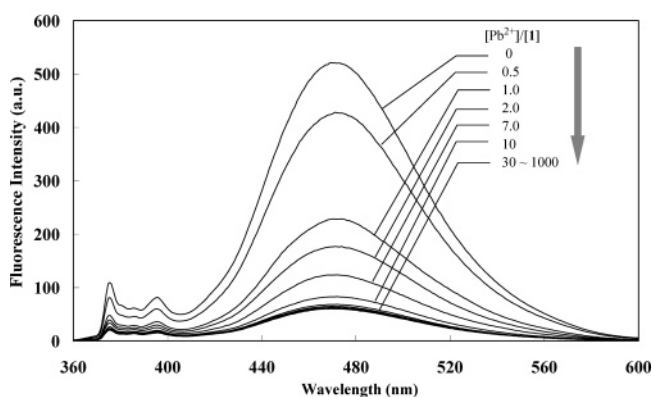
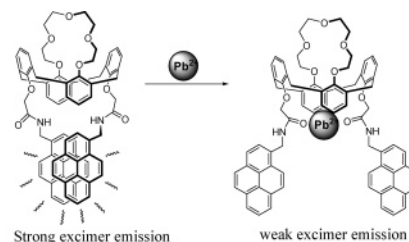
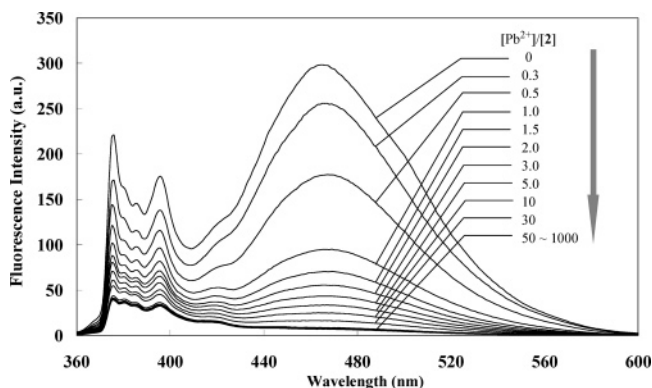
(a) (b) (c) (d)

Figure 1. Photograph of the quenched emission of **1** in MeCN. (a) Only **1** and in the presence of (b) K⁺, (c) Ca²⁺, and (d) Pb²⁺.

yields. The ester groups were hydrolyzed to give the corresponding calix[4]arene dicarboxylic acids **5** and **8** in moderate yields. Reaction of **5** and **8** with thionyl chloride to give the acid chlorides followed by amination with 1-pyrenemethylamine hydrochloride afforded fluorescent chemosensors **1** and **2** in 46 and 35% yields, respectively. In **1**, there are both polyether and amide binding sites for metal ion complexation, whereas **2** has only the latter.

We first probed the metal ion binding abilities of **1** and **2** based on fluorescence changes of their MeCN solutions produced by addition of perchlorate salts of the alkali metal cations, Ag⁺, Ca²⁺, Mg²⁺, Pb²⁺, and Zn²⁺. The results are presented in Table 1. In the absence of metal ion, the two pyrene units in **1** and **2** exhibit strong monomer ($\lambda_{em} = 375$ nm) and excimer ($\lambda_{em} = 470$ nm) bands. The latter is attributed to two facing pyrene units in an intramolecular π - π stacked arrangement under UV irradiation, which will be discussed later. The relative ratios of excimer to monomer ($I_{excimer}/I_{monomer}$) bands for **1** and **2** are 4.6 and 1.52, respectively. Presumably, the larger ratio for **1** results from its greater conformational rigidity compared to **2**.

Addition of Pb²⁺ to a solution of **1** markedly diminished the fluorescence intensities of both the pyrene monomer and excimer bands (Figure 1), with a more pronounced effect on the latter. The emission of **2**, which has only amide binding sites, was also strongly quenched by Pb²⁺ and to a lesser extent by Ag⁺ and Zn²⁺ (Table 1). These results suggest that Pb²⁺ is complexed by the two amide groups of each fluorophore, strongly quenching the emission intensity, but not by the crown-5 unit of **1**. The monomer fluorescence quenching can be explained as reverse PET when Pb²⁺ ion is bound to the two carbonyl oxygen atoms with the pyrene unit behaving as a PET donor to the carbonyl group,^{28,29} as well as a heavy metal effect.³⁰ Quenching of the excimer emission is rationalized as resulting from a conformational change caused by two outward-facing amide

**Figure 2.** Effect of added Pb²⁺ on the fluorescence emission spectra of **1** in MeCN. (The excitation wavelength was 344 nm.)**Figure 3.** Effect of added Pb²⁺ on fluorescence emission spectra of **2** in MeCN. (The excitation wavelength was 344 nm.)

carbonyl groups turning inward to bind with Pb²⁺. In this conformation, parallel stacking of the two pyrene units is no longer possible (see Figure 2) under UV irradiation, which will be discussed later more in detail.

Figures 2 and 3 show the fluorescence changes for solutions of **1** and **2**, respectively, in MeCN with increasing Pb²⁺

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concentration. From the data, association constants for complexation of Pb^{2+} by **1** and **2** in MeCN were calculated to be 4.4×10^5 and $5.2 \times 10^5 \text{ M}^{-1}$, respectively.³¹ In contrast, the addition of K^+ or Rb^+ to a solution **1** in MeCN gave little fluorescence change since these alkali metal cations are bound by the crown-5 ring.³² Selective K^+ binding by the fluorophore-free crown-5 ring was also shown by K^+ titration into a solution of the $\mathbf{1}\cdot\text{Pb}^{2+}$ complex (vide infra).

When a metal ion is bound by **1**, which has two different recognition sites, the metal ion chooses the more favorable binding location. The two amide oxygen atoms prefer binding with Pb^{2+} , resulting in a conformational change that produces excimer quenching. On the other hand, the addition of K^+ , which is suitable for coordination by the polyether unit of **1**, hardly affects the excimer stability, and little change in its emission intensity is observed. Metal ion-induced chemical shift changes in the ^1H NMR spectra show that K^+ is bound to the crown ether ring of **1** and Pb^{2+} to the two amide oxygen atoms (Figure S2). In the presence of 10 equiv of K^+ , chemical shifts of protons $\text{H}_i\text{--H}_1$ on the crown-5 ring of **1** change significantly, and the pyrene- CH_2 protons are shifted upfield by 0.18 ppm. In addition, the peak for H_g in the OCH_2CO unit is little influenced, indicating that K^+ is complexed by **1** via the crown ether ring. On the other hand, addition of 10 equiv of Pb^{2+} to **1** shifts the pyrene- CH_2 and OCH_2CO protons downfield by 0.26 and 0.73 ppm, respectively, suggesting that the amide carbonyl groups are involved in complexation with Pb^{2+} . The chemical shift change of the amide NH provides additional evidence for Pb^{2+} binding by the two amide units with a 1.12 ppm downfield shift in the presence of Pb^{2+} , but just 0.24 ppm in the presence of K^+ . For the aromatic protons $\text{H}_a\text{--H}_d$, downfield shifts of H_c ($\Delta\delta = 0.20$) and H_d ($\Delta\delta = 0.36$) are attributable to π -metal complexation between meta- and para-carbons and Pb^{2+} .

With regard to cation exchange based upon discrimination between these K^+ and Pb^{2+} , we observed an interesting on-off switching process. When K^+ was titrated into a solution of $\mathbf{1}\cdot\text{Pb}^{2+}$ complex, both the excimer and monomer bands gradually reformed and then became saturated upon addition of about 30 equiv of K^+ (Figure 4). It appears that this exchange process for 1:1 complexation is due not only to an electrostatic repulsion between the two metal ions, but also to an allosteric effect.

In the reverse of this metal ion exchange process, Pb^{2+} was titrated into a solution of $\mathbf{1}\cdot\text{K}^+$ complex, producing the fluorescence changes shown in Figure 5. Once again metal ion exchange is evident. However, it was observed that addition of Pb^{2+} slowly liberated K^+ from the polyether binding site of $\mathbf{1}\cdot\text{K}^+$ complex compared with the release of Pb^{2+} upon addition of K^+ to the $\mathbf{1}\cdot\text{Pb}^{2+}$ complex. For the former, the fluorescence quenching continued to increase even after more than 500 equiv of Pb^{2+} were added. This suggests that K^+ is complexed stronger and faster by the crown-5 ring than is Pb^{2+} by the two amide oxygen atoms of **1**.

When K^+ was added to a solution of $\mathbf{2}\cdot\text{Pb}^{2+}$ complex, the fluorescence intensity scarcely changed, as shown in Figure 6,

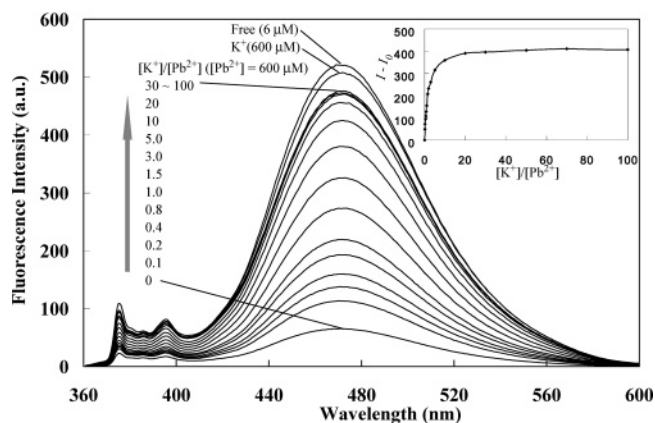
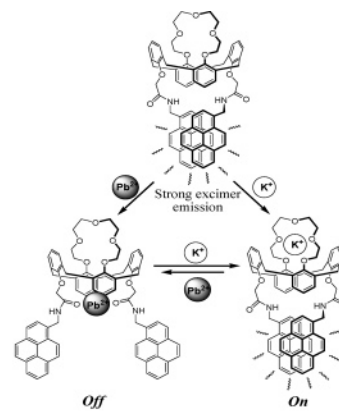


Figure 4. Fluorescence emission changes for the $\mathbf{1}\cdot\text{Pb}^{2+}$ complex in MeCN upon addition of K^+ . (The excitation wavelength was 344 nm.)

implying that no cation exchange occurred in **2** since the two propyloxy groups are unable to function as a K^+ recognition site. This observation supports the contention that on-off switching based on metal-ion exchange requires more than one cation binding site.

We also performed ab initio calculations to probe the fluorescence behavior of **1** in the presence of different metal ion species. The calculations were carried out at the level of density functional theory (DFT) with Becke-3-Lee-Yang-Parr (B3LYP) exchange functionals using the Gaussian 98 suite of programs.³³ The 3-21G basis sets were used except for Pb^{2+} , where the LANL2DZdp effective core potential (ECP) was utilized. Figure 7 presents energy-minimized structures of fluorescence chemosensor **1** and its complexes with Pb^{2+} and K^+ . There are two different binding sites in the host molecule, crown ether, and amide. For $\mathbf{1}\cdot\text{Pb}^{2+}$, the binding energy for the amide site is much larger than that for the crown ether site by ~ 29.76 kcal/mol; while for $\mathbf{1}\cdot\text{K}^+$, the binding energies for the ether and amide sites are almost the same, although the ether

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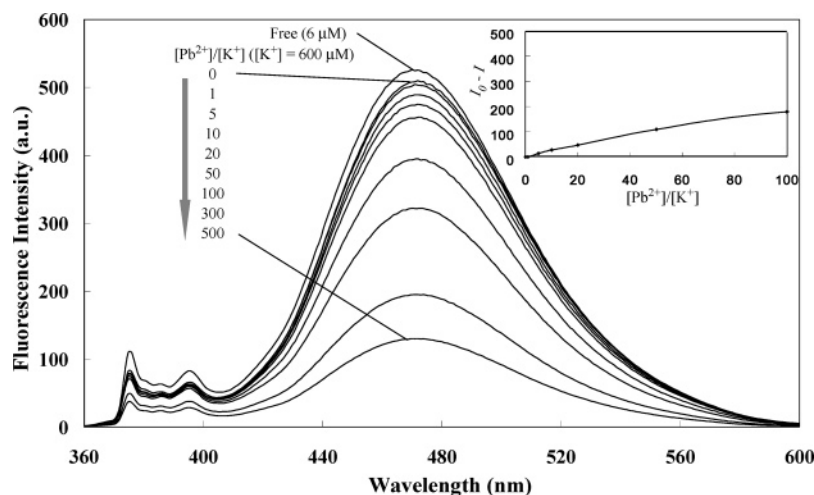


Figure 5. Fluorescence emission changes for the $1 \cdot K^+$ complex in MeCN upon addition of Pb^{2+} . (The excitation wavelength was 344 nm.)

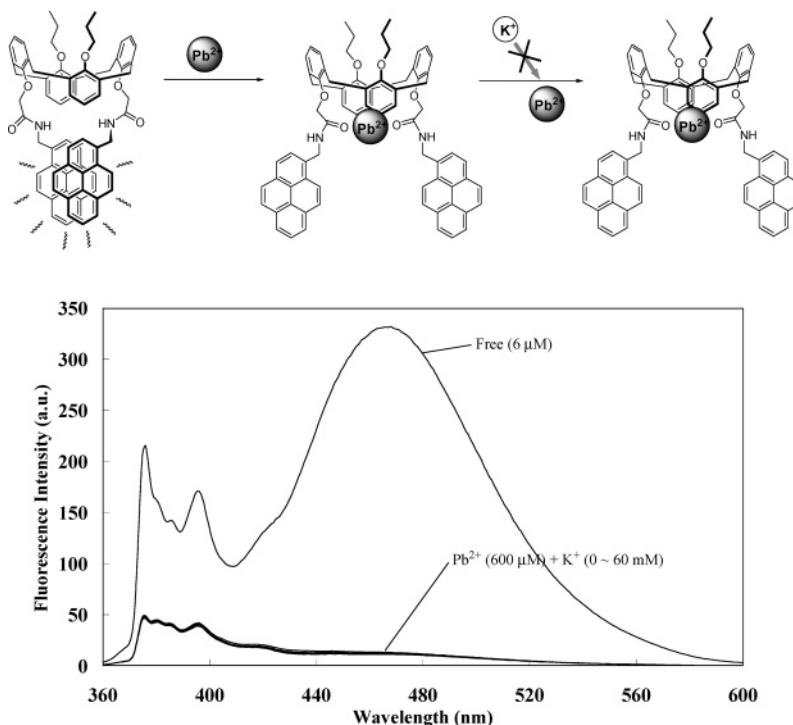


Figure 6. Fluorescence emission spectra for the $2 \cdot Pb^{2+}$ complex in MeCN upon addition of K^+ . (The excitation wavelength was 344 nm.)

site gives slightly stronger binding affinity by ~ 0.13 kcal/mol. The calculated binding preference is consistent with the experimental results that Pb^{2+} is complexed at the amide site and K^+ at the crown ether site.

To shed light on the variation of fluorescence intensity upon the addition of Pb^{2+} and K^+ to **1**, we investigated the frontier molecular orbitals of **1** and its Pb^{2+} and K^+ complexes. The HOMO and LUMO for **1** are shown in Figure 8. The frontier molecular orbitals for the complexes are depicted in Figure S1 in the Supporting Information. The fluorescence intensity can be considered to be the excimer emission. Therefore, chemical systems whose excited states are stabilized can give strong emission. In this regard, we first assume that the excited states of the host molecule and its K^+ complex are stabilized through the pyrene–pyrene interactions, while its Pb^{2+} complex is not. This assumption can be justified from the frontier molecular orbitals because the general electronic transitions under UV

irradiation (with an excitation wavelength of 344 nm) are HOMO \rightarrow LUMO, HOMO \rightarrow LUMO2, HOMO \rightarrow LUMO3, or some transitions near them. (LUMO2 and LUMO3 represent the second and third LUMO, respectively.) In our previous work, it was found that these molecular orbitals could explain the electronic transitions quite reasonably.²⁶

In **1** and its complexes, the HOMO shows that most electron density resides in one of the pyrene moieties. However, the LUMOs for the Pb^{2+} complex reveal a remarkable difference from those for **1** and its K^+ complex. It is seen in Figure 8 that the excited states of **1** under UV irradiation can be stabilized by π – π interactions, which can be evidenced by the HOMO \rightarrow LUMO and HOMO \rightarrow LUMO3 transitions. Similarly, the excited states for the K^+ complex can be stabilized as implicated in the HOMO \rightarrow LUMO3 transitions. From this investigation of the molecular orbitals, it is apparent that the excited state

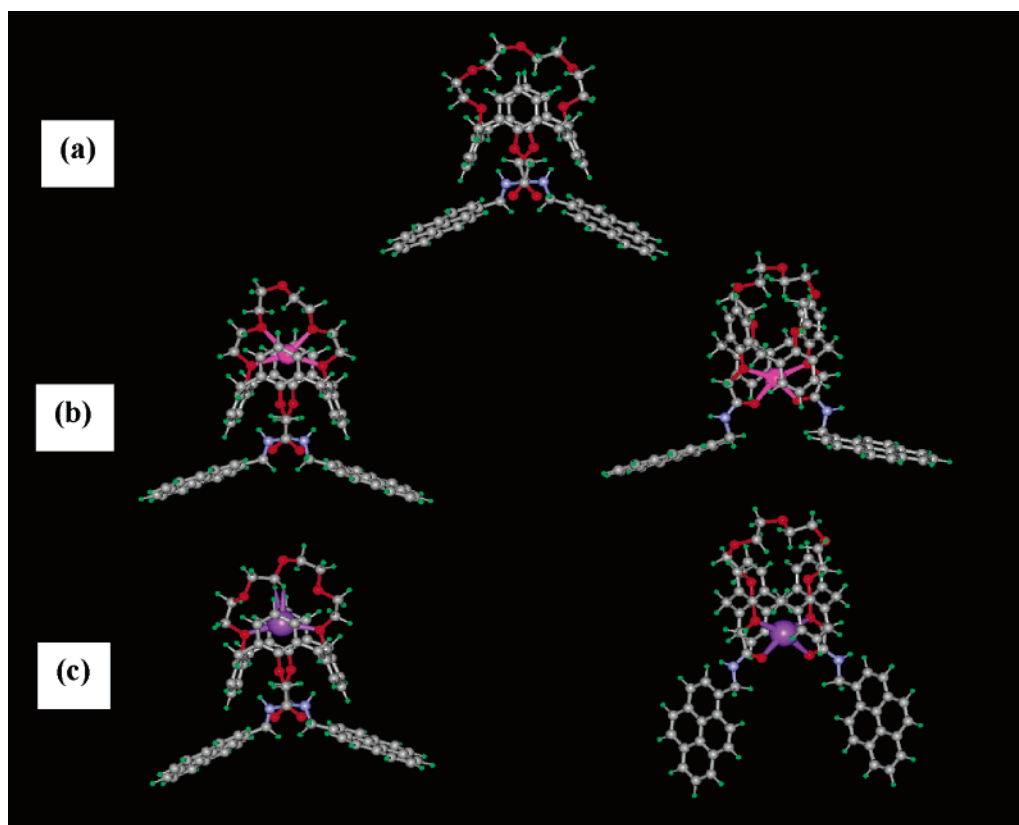


Figure 7. B3LYP/3-21G predicted structures for (a) **1**, (b) its Pb^{2+} complex, and (c) its K^{+} complex. For the complexes, structures on the left are for crown ether binding, and the structures on the right are for amide binding.

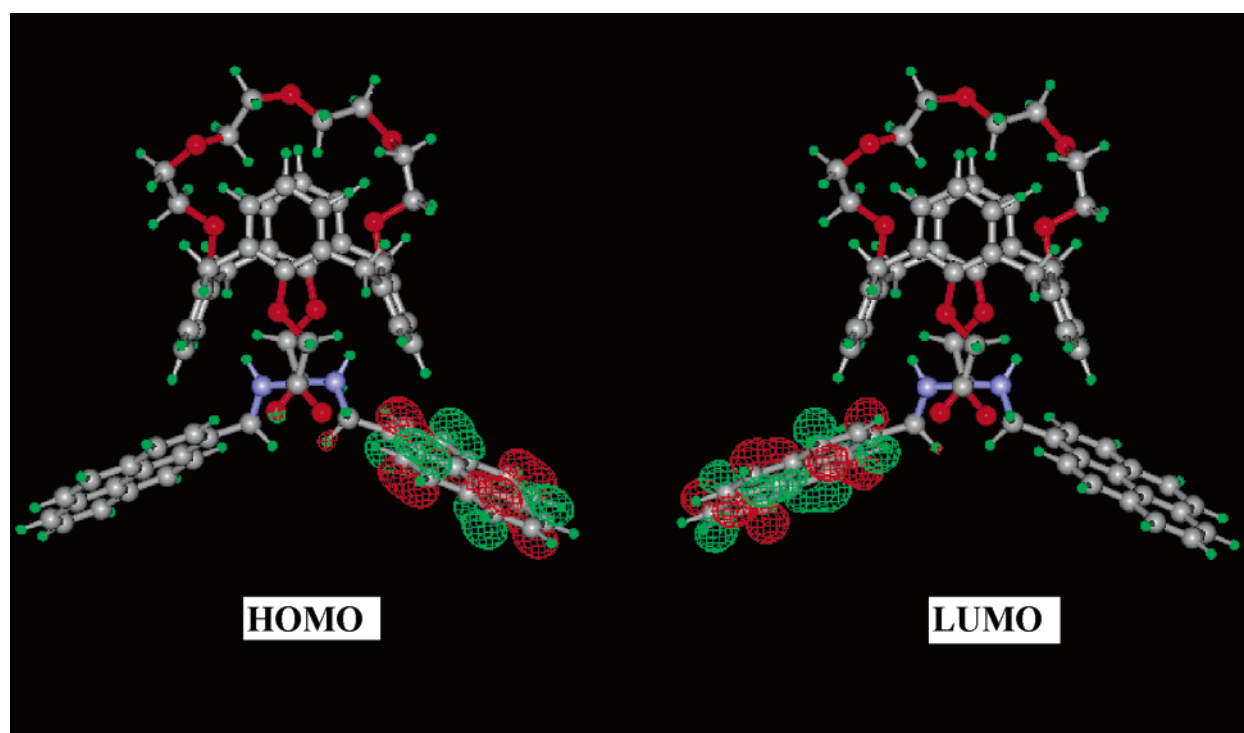


Figure 8. Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of **1**.

(LUMO) of one of the two pyrene units shows a strong interaction with the ground state (HOMO) of the other pyrene unit through the π - π stacking in **1** and the **1**· K^{+} complex. A steady-state fluorescence spectroscopy experiment showed that

the intensities of both monomer and excimer emissions increase upon addition of K^{+} , which excludes intramolecular excimer emission from π - π stacking of the pyrene rings in the free state and supports intramolecular excimer emission by interac-

tion of an excited pyrene (Py*) with a ground-state pyrene (Py).^{14,15} However, the Pb²⁺ complex does not show such π – π interactions up to LUMO7.

Conclusions

A new fluorescent chemosensor with two different cation binding sites on lower rims of an 1,3-alternate calix[4]arene framework is synthesized. In the free ligand, two pyrene moieties linked to the cation recognition units composed of the amide groups form a strong excimer. The emission spectrum changes induced by the addition of metal cations indicate that the **1** shows high selectivities for Pb²⁺ and K⁺ over other metal ions investigated, while **2** with propyl groups instead of a crown-5 ring shows selectivity only for Pb²⁺. Upon addition of Pb²⁺ ion to a solution of **1** in MeCN, both monomer and excimer bands were strongly quenched because of reverse PET from the pyrene unit to the amide group and a geometrical change of the two pyrene amide groups, respectively. On the other hand, addition of K⁺ to a solution of **1** gave no change in emission intensity because K⁺ is entrapped not by the amide group but by the crown-5 ring. For **1**, the excimer fluorescence is quenched by Pb²⁺, but revived by the addition of K⁺ to the Pb²⁺ ligand complex. Thus, the metal ion exchange produces an on–off switchable fluorescence. These experimental observations of **1** and its complexes are rationalized by the electron densities of the frontier molecular orbitals, HOMO and LUMOs. For **1** and **1**·K⁺, the two separated pyrene groups have accumulated electron densities for HOMO and LUMOs, whereas for **1**·Pb²⁺, such LUMOs were not found. Thus, the excited states for **1** and **1**·K⁺ can be stabilized by π – π interactions, which are evident from the HOMO \rightarrow LUMO and/or HOMO \rightarrow LUMO3 transitions. However, the **1**·Pb²⁺ does not show such π – π interactions up to LUMO7.

Experimental Section

Compound **3** was prepared following the literature procedure.²⁷

25,27-Bis(ethoxycarbonylmethoxy)calix[4]crown-5 (4). Under nitrogen, **3** (1.00 g, 1.68 mmol), tetraethylene glycol ditosylate (0.93 g, 1.85 mmol), and Cs₂CO₃ (1.64 g, 5.04 mmol) in 100 mL of MeCN were refluxed for 24 h and evaporated in vacuo. To the resulting white solid, 5% aqueous HCl solution (100 mL) and CH₂Cl₂ (50 mL) were added. The organic layer was washed three times with water (50 mL), dried over MgSO₄, and evaporated in vacuo to give a white solid. Chromatography on silica gel with EtOAc–hexane (1/3) as eluent gave 1.08 g (85%) of **4** as a white solid. mp: 170 °C. IR (KBr): 1669 cm⁻¹. ¹H NMR (400 MHz, CDCl₃): δ 7.15–7.11 (dd, 8 H, ArH_m, *J* = 8.21 Hz), 6.92–6.88 (t, 2 H, ArH_p, *J* = 7.47 Hz), 6.86–6.82 (t, 2 H, ArH_p), 4.16–4.12 (d, 4 H, ArCH₂Ar, *J* = 16.14 Hz), 4.05–4.00 (q, 4 H, COOCH₂CH₃), 3.87–3.83 (d, 4 H, ArCH₂Ar, *J* = 16.11 Hz), 3.66–3.56 (m, 12 H, OCH₂CH₂O), 3.36 (s, 4 H, ArOCH₂CO), 3.17–3.14 (t, 4 H, OCH₂CH₂O, *J* = 6.76), 1.19–1.15 (t, 6H, COOCH₂CH₃, *J* = 7.12). ¹³C NMR (100 MHz, CDCl₃): 171.2, 161.8, 158.2, 129.1, 126.9, 126.5, 121.8, 121.1, 76.2, 73.6, 70.9, 70.5, 59.2, 38.7, 22.1, 13.6 ppm. FAB MS *m/z* (M⁺) calcd 754.8, found 755.5. Anal. Calcd for C₄₄H₅₀O₁₁: C, 70.01; H, 6.68. Found: C, 70.04; H, 6.70.

25,27-Bis(hydroxycarbonylmethoxy)calix[4]crown-5 (5). A solution of **4** (0.50 g, 0.66 mmol) and NaOH (0.25 g, 6.25 mmol) in THF (5 mL), ethanol (10 mL), and water (5 mL) were refluxed for 12 h and evaporated in vacuo. The residue was dissolved in EtOAc, and the solution was washed twice with 20% HCl and then three times with water. The organic layer was dried over MgSO₄ and evaporated in vacuo to yield 0.43 g (93%) of **5** as a white solid. mp: 273–280 °C. IR (KBr): 1693 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 7.19–7.15 (d, 4

H, ArH_m, *J* = 7.40 Hz), 7.07–7.04 (d, 4 H, ArH_m, *J* = 7.00 Hz), 6.98–6.87 (m, 4 H, ArH_p), 4.13 (s, 4 H, ArOCH₂CO), 4.01–3.93 (d, 4 H, ArCH₂Ar, *J* = 16.4 Hz), 3.88–3.79 (d, 4 H, ArCH₂Ar, *J* = 16.8 Hz), 3.58–3.53 (m, 12 H, OCH₂CH₂O), 3.19–3.13 (t, 4 H, OCH₂CH₂O, *J* = 5.80). ¹³C NMR (50 MHz, CDCl₃): 169.5, 156.7, 154.5, 134.5, 130.7, 129.2, 125.5, 79.4, 73.3, 71.7, 70.7, 69.7, 68.0, 38.6 ppm. FAB MS *m/z* (M⁺) calcd 698.8, found 699.0. Anal. Calcd for C₄₄H₄₂O₁₁: C, 68.75; H, 6.06. Found: C, 68.79; H, 6.04.

25,27-Bis(chlorocarbonylmethoxy)calix[4]crown-5 (6). A solution of **5** (0.30 g, 0.43 mmol) and SOCl₂ (3 mL) in dry toluene (5 mL) was stirred and refluxed for 4 h. The SOCl₂ and toluene were removed by simple distillation. The residue was dissolved in dry THF (5 mL), and the solution was evaporated in vacuo to remove the residual SOCl₂. The resulting white solid was used directly for the next reaction.

25,27-Bis(ethyl acetoethoxy)-26,28-dipropylcalix[4]arene (7). A mixture of **3** (2.00 g, 2.50 mmol), Cs₂CO₃ (2.44 g, 7.49 mmol), and acetonitrile (60 mL) was stirred magnetically for 20 min, and then 1-iodopropane (2.28 g, 13.4 mmol) was added. The reaction mixture was refluxed for 2 days and evaporated in vacuo. The residue was extracted with CH₂Cl₂, and the organic solution was washed with water, dried over MgSO₄, and evaporated in vacuo to afford a slightly colored residue. Recrystallization from CH₂Cl₂–hexane produced 1.12 g (49%) of **7** as crystalline solid. mp: 142 °C. IR (KBr): 1759 cm⁻¹. ¹H NMR (CDCl₃): δ 7.09 (d, 4 H, ArH_m, *J* = 7.6 Hz), 7.00 (d, 4 H, ArH_m, *J* = 7.6 Hz), 6.72 (t, 2 H, ArH_p, *J* = 7.6 Hz), 6.71 (t, 2 H, ArH_p, *J* = 7.6 Hz), 4.12 (q, 4 H, OCH₂, *J* = 7.1 Hz), 3.89 (d, 4 H, ArCH₂Ar, *J* = 14.8 Hz), 3.68 (d, 4 H, ArCH₂Ar, *J* = 14.8 Hz), 3.57 (s, 4 H, OCH₂CO), 3.51 (t, 4 H, OCH₂, *J* = 7.4 Hz), 1.45 (sextet, 4 H, CH₂, *J* = 7.4 Hz), 1.23 (t, 6 H, CH₃, *J* = 7.1 Hz), 0.84 (t, 6 H, CH₃, *J* = 7.4 Hz). ¹³C NMR (CDCl₃): 170.29 (C=O), 157.18, 155.40, 134.56, 133.84, 130.44, 130.27, 122.70, 122.54 (Ar), 73.66, 69.10, 60.64 (OCH₂), 23.14 (CH₂), 14.35, 10.44 (CH₃) ppm. FAB MS *m/z* (M⁺) calcd 680.8, found 681.0. Anal. Calcd for C₄₂H₄₆O₈: C, 74.09; H, 7.11. Found: C, 74.17; H, 7.04.

25,27-Bis(hydroxycarbonylmethoxy)-26,28-dipropylcalix[4]arene (8). Compound **8** was synthesized by modification of the procedure reported above for **5**. White solid (93%). mp: 265–270 °C. IR (KBr): 1701 cm⁻¹. ¹H NMR (200 MHz, CDCl₃–CD₃SOCD₃): δ 7.09–7.06 (d, 4 H, ArH_m, *J* = 6.40 Hz), 7.06–7.03 (d, 4 H, ArH_m, *J* = 5.60 Hz), 6.87–6.77 (m, 4 H, ArH_p), 4.00–3.81 (m, 4 H, ArOCH₂CO; 8 H, ArCH₂Ar), 3.49–3.42 (t, 4 H, ArOCH₂CH₂, *J* = 6.60), 1.35–1.25 (sextet, 4 H, CH₂CH₂CH₃), 0.74–0.67 (t, 6 H, CH₂CH₂CH₃, *J* = 7.20). ¹³C NMR (50 MHz, CDCl₃–CD₃SOCD₃): 170.4, 156.7, 154.4, 133.8, 133.4, 129.8, 129.4, 72.2, 67.5, 37.3, 22.7, 10.2 ppm. FAB MS *m/z* (M⁺) calcd 624.7, found 625.0. Anal. Calcd for C₃₈H₄₀O₈: C, 73.06; H, 6.45. Found: C, 73.07; H, 6.47.

25,27-Bis(chlorocarbonylmethoxy)-26,28-dipropylcalix[4]arene (9). Compound **9** was prepared by modification of the procedure reported above for **6**. The white solid was used for further reaction without purification.

25,27-Bis[*N*-(1-pyrenylmethyl)aminocarbonylmethoxy]calix[4]crown-5 in the 1,3-Alternate Conformation (1). A solution of **6** (0.30 g, 0.41 mmol), 1-pyrenemethylamine hydrochloride (0.23 g, 0.86 mmol), and Et₃N (1.0 mL, 1.38 mmol) in 20 mL of dry THF was refluxed with stirring for 2 days and then evaporated in vacuo. The resulting solid was dissolved in CH₂Cl₂ (100 mL), and the organic layer was washed three times with water, dried over MgSO₄, and evaporated in vacuo. The crude product was chromatographed on silica gel with EtOAc–hexane (3/1) as eluent to give 0.21 g (46%) of **1** as a white solid. mp: 262–270 °C. IR (KBr): 3304, 1650 cm⁻¹. ¹H NMR (200 MHz, CDCl₃): δ 8.15–7.80 (m, 18 H, ArH, pyrene), 7.14–7.05 (m, 4 H, ArH_m; 2 H, ArH_p), 6.92–6.84 (t, 2 H, ArH_p, *J* = 7.2 Hz), 6.76–6.73 (d, 4 H, ArH_m, *J* = 7.20), 6.27–6.20 (t, 2 H, CONHCH₂, *J* = 7.40), 4.95–4.92 (d, 4 H, ArCH₂NH, *J* = 5.60), 3.72 (s, 8 H, ArCH₂Ar), 3.57–3.43 (m, 4 H, ArOCH₂CO; 12 H, OCH₂CH₂O), 3.34–3.28 (m, 4 H, ArOCH₂CH₂O, *J* = 5.80). ¹³C NMR (50 MHz, CDCl₃): 169.5,

157.5, 155.8, 135.6, 134.7, 132.6, 130.8, 129.2, 127.4, 126.9, 126.2, 125.8, 125.7, 125.5, 124.5, 124.4, 123.8, 77.4, 73.2, 71.8, 70.2, 38.8 ppm. FAB MS m/z (M^+) calcd 1125.3, found 1125.0. Anal. Calcd for $C_{74}H_{64}N_2O_9$: C, 78.98; H, 5.73. Found: C, 79.00; H, 5.76.

25,27-Bis[(*N*-(1-pyrenylmethyl)aminocarbonyl)methoxy]-26,28-dipropylloxycalix[4]arene in the 1,3-Alternate Confirmation (2).

Compound **2** was prepared by modification of the procedure given above for **1**. The crude product was purified by chromatography on silica gel with EtOAc–hexane (1:5) as eluent to give a 35% yield of **2**. mp: 221–230 °C. IR (KBr): 3300, 1669 cm^{-1} . 1H NMR (200 MHz, $CDCl_3$): δ 8.25–7.90 (m, 18 H, ArH, pyrene), 7.02–7.00 (m, 4 H, ArH_m; 2 H, ArH_p), 6.76–6.66 (m, 2 H, ArH_p; 4 H, ArH_m), 5.99–5.92 (t, 2 H, CONHCH₂, $J = 8.00$), 5.18–5.14 (d, 4 H, ArCH₂NH, $J = 6.20$), 3.65–3.30 (m, 4 H, ArOCH₂CO; 8 H, ArCH₂Ar; 4 H, ArCH₂NH; 4 H, ArOCH₂CH₂), 1.65–1.54 (sextet, 4 H, CH₂CH₂CH₃), 0.88–0.82 (t, 6 H, CH₂CH₂CH₃, $J = 5.2$). ^{13}C NMR (50 MHz, $CDCl_3$): 168.9, 157.4, 153.8, 134.6, 123.3, 131.7, 131.5, 130.9, 130.7, 130.0, 128.8, 127.8, 127.3, 126.8, 125.8, 125.2, 124.9, 124.5, 122.9, 122.6, 73.5, 40.1, 37.1, 23.2, 10.1 ppm. FAB MS m/z (M^+) calcd 1051.3, found 1051.0. Anal. Calcd for $C_{72}H_{62}N_2O_6$: C, 82.26; H, 5.94. Found: C, 82.30; H, 5.90.

General Procedure for Fluorescence Studies. Fluorescence spectra were recorded with a RF-5301PC spectrofluorophotometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in MeCN. Stock solutions of **1** and **2** (0.06 mM) were prepared in MeCN. For all measurements, excitation was at 344 nm with excitation and emission slit widths at 3 nm. Fluorescence titration experiments were performed using 6 μM solutions of **1** and **2** in MeCN and various concentrations of Pb^{2+} perchlorate in MeCN. After calculating the

concentrations of the free ligands and complexed forms of **1** and **2** from the fluorescence titration experiments, the association constants were obtained using the computer program ENZFITTER.³¹

Computational Methods

The molecular complexes of **1** with Pb^{2+} (**1**· Pb^{2+}) and K^+ (**1**· K^+) as well as **1** were optimized by DFT calculations using the nonlocal exchange correlation functional of Becke's three parameters employing the Lee–Yang–Parr functional (B3LYP) with LANL2DZdp ECP for Pb^{2+} and 3-21G basis sets for others using the Gaussian 98 program. The two different complexes were considered in the geometry optimization depending on the two binding sites, crown ether and amide. The interaction energy is simply obtained by the energy of the complex subtracted by the sum of energies of the constituents. Generally, the basis sets superposition error (BSSE) correction should be included to obtain an accurate interaction energy. However, in this study, the interaction energy itself is not the main problem, and the interaction is very strong mainly because of the electrostatic interactions; hence, the BSSE may contribute in minor manner. Thus, the BSSE is not considered in this study. To obtain some insights on the intensity of the excimer emission, the stability of the excited states for **1**· Pb^{2+} , and **1**· K^+ are inferred from the electron densities of the frontier molecular orbitals.

Supporting Information Available: Additional figures (Figures S1–S3). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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