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On–Off Switchable Binuclear Chemosensor Based on Thiacalix[4]crown Armed with Pyrene Moieties

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A new fluorescent "on–off" switchable chemosensor **2** based on a thiacalix[4] arene with a 1,3-*alternate* conformation and two different types of cation binding sites has been synthesized. Two pyrene moieties linked to a cation recognition unit composed of two imine groups form a strong excimer in solution. Of the metal ions tested, the fluorescence of **2** was strongly quenched by Hg^{2+}, Pb^{2+} and Cu^{2+} ions. The fluorescence was revived by the addition of only K^+ to the Cu^{2+} ligand complex. Thus, metal-ion exchange triggers an "on–off" switchable fluorescent chemosensor.

Introduction

Recently there has been a lot of interest in the design, synthesis and evaluation of fluorescent sensors that selectively complex metal ions and anions because of their potential analytical applications in many fields, for example, chemistry, medicine, biology and the environment.[1,2] Basically, a fluorescent chemosensor consists of an ion recognition unit (ionophore) attached to a fluorogenic unit (fluorophore)[2b,3] that converts a binding signal from the ionophore unit into a highly sensitive light signal. Thus, while designing fluorescent sensors the recognition unit and fluorophore should be carefully examined because the recognition unit is responsible for the selectivity and binding efficiency of the chemosensor and the fluorophore is responsible for signalling the binding event. Of the different fluorogenic units, pyrene is the most useful because of its efficient and sensitive monomer emission in the range of 370–430 nm and its excimer emission at around 480 nm.[2c,4] The intensity ratio of the excimer-to-monomer emission (I_E/I_M) is very sensitive to conformational change and the guest ion (cation and anion) concentration,[1,4b,5] and hence it is a very informative tool in sensing systems. Calixarenes with appropriately appended groups are good candidates for cation[6] recognition because they have been shown to be highly specific ligands[6] and their potential as sensing agents has received increasing interest.[7] Of the various calix[4]arene derivatives, calix[4]crowns are very interesting because they can have differing numbers of donor atoms of different nature in the crown ring, thus making it possible to accommodate a variety of guests.[8] Kim and Quang[9] recently reported calix[4]arene-derived fluorescent probes, highlighting the importance of fluorescent chemosensors. Thiacalix[4]arenes,[10] reported as the second generation of calixarenes, are good receptors for soft- and transition-metal ions.[11] Thus, they have been extensively used for the recognition of cations[11] and anions,[12] and their potential applications as fluorescence sensing agents have received much interest.[11] A 1,3-*alternate* thiacalix[4]crown provides a crown ether ring for metal-ion complexation with potential for additional binding by cation–π interactions between the two rotated benzene rings and a polyether-complexed metal ion.[13] In most fluorescent sensors based on calix[4]-arenes and thiacalix[4]arenes, the cation-binding involves photophysical changes such as photoinduced electron transfer (PET),[14] photoinduced charge transfer (PCT),[15] the formation of a monomer/excimer[16] and energy transfer.[17]

Our research involves the design, synthesis and evaluation of calix[4]arene- and thiacalix[4]arene-based receptors that are selective for soft-metal ions[18] and anions.[19] We recently reported a ratiometric[20] fluorescent sensor for mercury ions based on a *partial cone* conformation of the calixarene, which behaves as a NOR logic gate with a YES logic function, and a ratiometric[21] fluorescent sensor for copper based on a thiacalix[4]arene of the 1,3-*alternate* conformation, which behaves as an INHIBIT logic gate with NOT and YES functions. Neither of the receptors exhibited any "on–off" switchable behaviour. However, organic molecules that can undergo "on–off" switchable behaviour under the influence of appropriate stimulation are predicted to open new perspectives for the realization of artificial functions at the molecular level.[22] The controlling of these processes at a molecular level using external stimuli is an interesting scientific challenge. Molecules that involve intra-

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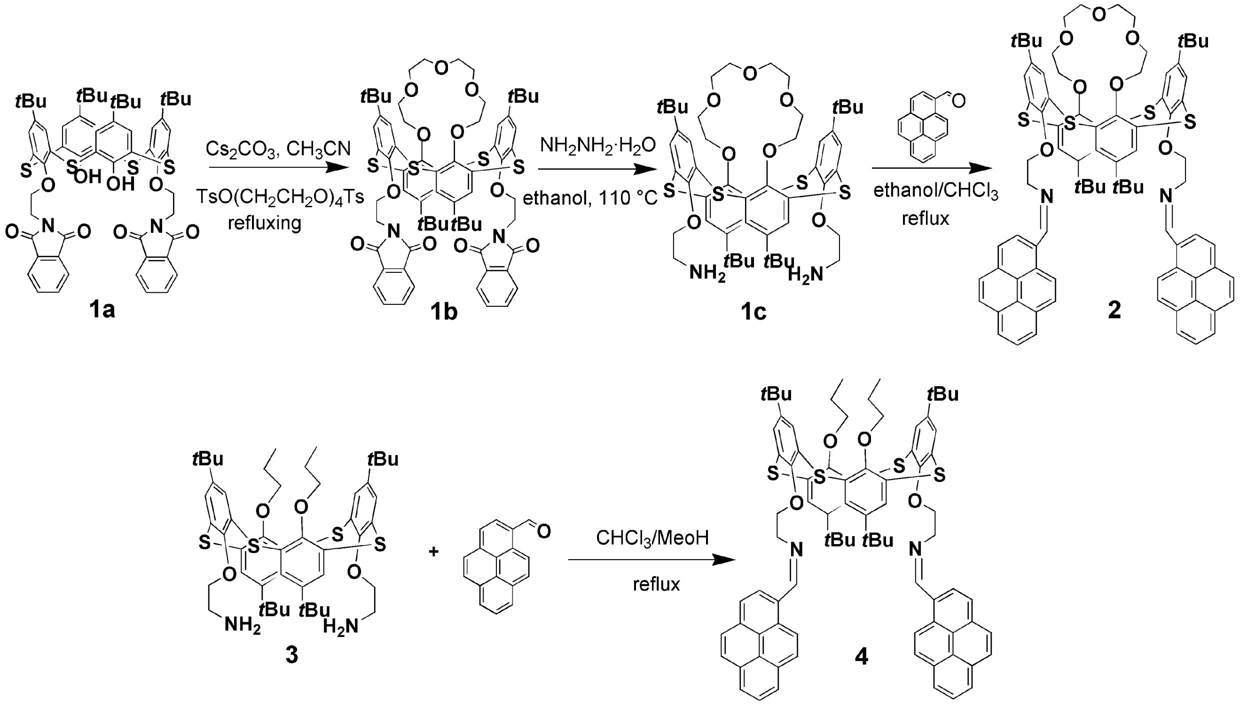
molecular ion exchange and exhibit switching behaviour have also been reported.[23] In these sensors, cation- and anion-exchange processes are ascribed not only to the repulsion between ions, but also to an allosteric effect.[24] In view of the significance of such organic molecules, we have now prepared a novel fluorescent "on–off" switchable chemosensor that undergoes fluorescence quenching in the presence of Hg^{2+}, Pb^{2+} and Cu^{2+} ions, but the fluorescence is revived by the addition of only K^+ to the Cu^{2+} ligand complex. Thus, metal-ion exchange triggers an "on–off" switchable, fluorescent chemosensor. Kim and co-workers[25,26] have reported some examples of "on–off" (Pb^{2+}/K^+, Pb^{2+}/Ca^{2+}) fluorescence switches of calix[4]arenes, however, "on–off" (Cu^{2+}/K^+) switchable chemosensors based on calix[4]arenes and thiacalix[4]arenes are unprecedented. While this work was in progress, Chung and co-workers reported[27] an "on–off" (Pb^{2+}/K^+) switchable chemosensor based on a triazole-modified calix[4]crown.

Results and Discussion

Thiacalix[4]arene receptors **2** and **4** were prepared from known precursors **1a**[28] and **3**, respectively.[18c] Treatment of compound **1a**[28] with tetraethylene glycol ditosylate in dry acetonitrile using Cs_2CO_3 as a base gave **1b** in 50% yield. Compound **1b** was assigned the 1,3-*alternate* conformation on the basis of ^1H NMR chemical shifts and our own recently reported results.[18b] The *tert*-butyl and aromatic protons in the 1,3-*alternate* conformation are deshielded, whereas those in the cone conformer are shielded by the attached phenyl rings. As a result, two singlets for the 1,3-*alternate* conformation are expected at lower field [1.28–1.39 ppm (*tert*-butyl), 7.29–7.58 ppm (aromatic)], whereas for the cone conformation they are at a higher field [0.72–1.27 ppm (*tert*-butyl), 6.96–7.58 ppm (aromatic)]. Apart from this, the OCH_2 and NCH_2 moieties of the 1,3-*alternate* conformation are shielded by the adjacent phenyl rings and thus appear at a higher field (3.36–3.90 and 2.31–3.45 ppm) than those of the cone conformer (4.87 and 4.44 ppm). The hydrazinolysis of compound **1b** in ethanol gave diamine **1c** in 80% yield. Condensation of diamine **1c** with 2.1 mol-equiv. of 1-pyrenecarbaldehyde in a mixture of chloroform and ethanol (1:1) at reflux gave thiacalix[4]arene receptor **2** in 70% yield. By using the same procedure, we prepared thiacalix[4]arene receptor **4** by condensing **3**[18c] with 1-pyrenecarbaldehyde (Scheme 1). The structures of thiacalix[4]arene receptors **2** and **4** were confirmed from their spectroscopic and analytical data (see pages S3–S10, S19 and S20 of the Supporting Information). Receptor **2** contains both the crown-5 ring and the imine moieties as metal-ion binding sites, whereas compound **4** contains only imine moieties as metal-binding sites.

The cation-binding properties of compounds **2** and **4** were investigated by UV/Vis and fluorescence spectroscopy. The titration experiments were carried out in MeCN/CH_2Cl_2 (1:1) by adding aliquots of different metal ions. The absorption spectrum of **2** (1×10^{-5} M) is characterized by typical absorption bands of pyrene at λ = 286, 306, 344, 360 and 395 nm in MeCN/CH_2Cl_2 (1:1). Of the metal ions tested (Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, K^+, Na^+ and Li^+), a new band is formed at 457 nm on addition of Cu^{2+} (Figure 1), Hg^{2+} (see Figure S1 on page S12 of the Supporting Information) and Pb^{2+} ions (see Figure S2 on page S12). The formation of a new band at 457 nm was



Scheme 1.

attributed to the interaction of these ions with the imino nitrogen atoms, leading to intramolecular charge transfer (ICT) from the pyrene moiety to the imino group. Similar results were obtained when aliquots of these three metal ions were titrated with receptor **4** (see pages S13 and S14 of the Supporting Information).

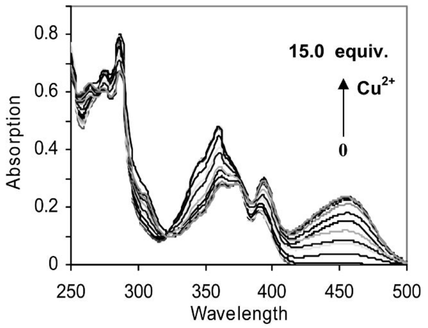


Figure 1. UV/Vis spectra of **2** (1×10^{-5} M) in the presence of Cu^{2+} ions (0–15.0 equiv.) in $MeCN/CH_2Cl_2$ (1:1).

In the fluorescence spectra, the pyrene groups of compounds **2** and **4** exhibited typical excimer emission bands centred at 490 nm and a weak monomer emission at 396 nm. The formation of excimer bands indicate that compounds **2** and **4** exist in stacked or folded conformations with the two pyrene units very close to each other. Upon addition of various metal ions, that is, Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, K^+, Na^+ and Li^+ as their perchlorate salts, to solutions of compounds **2** and **4**, a change in the fluorescence behaviour was observed. The results are shown in Figure 2. It was observed that the fluorescence of both receptors **2** and **4** (2.5 μM) was strongly quenched by the addition of Hg^{2+}, Pb^{2+} and Cu^{2+} ions. However, it was enhanced with K^+ ions in the case of receptor **2**. These results confirm that Hg^{2+}, Pb^{2+} and Cu^{2+} are recognized by the pyrenyl nitrogen atoms. The fluorescence quenching of monomer emission induced by Hg^{2+}, Pb^{2+} and Cu^{2+} in the case of receptors **2** and **4** can be ascribed to reverse PET[25] from the pyrene unit to the nitrogen[29] atom, the electron density of which is diminished by metal complexation. The excimer quenching is a result of a conformational change that occurs during the binding of these metal ions to the two nitrogen atoms. In this changed conformation, it is not possible for the pyrene groups to stack in parallel. The fluorescence spectra of **2** (2.5 μM) at various concentrations of Cu^{2+} are shown in Figure 3. The fluorescence intensity of both the monomer and excimer bands gradually decreased as the concentration of Cu^{2+} was increased from 0 to 8 equiv. Fitting the changes in the fluorescence spectra of compound **2** with copper ions by using the non-linear regression analysis program SPECFIT[30] gave a good fit and demonstrated that a 1:1 stoichiometry of the host and guest was the most stable species in the solution with a binding constant ($\log\beta_1$) of 5.70. The method of continuous variation (Job's plot) was also used to prove the 1:1 stoichiometry of the host and guest.[31] Similar fluorescence behaviour and 1:1 stoichiometry was observed for the addition of Pb^{2+} and Hg^{2+} to receptor **2** (see Figures S6 and S7 on page S15). The binding of Hg^{2+} and Pb^{2+} to **2** has also been proved by NMR spectroscopy (see pages S16–S18) as the imine protons undergo a downfield shift of 1.64 and 1.65 ppm, respectively. The $\log\beta_1$ values for $\mathbf{2}\cdot Pb^{2+}$ and $\mathbf{2}\cdot Hg^{2+}$ complexes were found to be 6.15 and 6.54, respectively. However, in contrast, the addition of 94 equiv. of K^+ to a solution of **2** in $MeCN/CH_2Cl_2$ (1:1) gave 21 % fluorescence enhancement (see page S21). The reason for the increase in the intensity of the excimer band at 490 nm is due to the fact that the K^+ ions bind to the polyether chain and as a result the photoinduced electron transfer to the photoexcited pyrene dimer is suppressed. The binding of the K^+ ions to the crown-5 ring is also supported by a ^1H NMR study in which the 3-H, 4-H, 5-H and 6-H protons of the crown-5 ring are shifted downfield by 0.22, 0.35, 0.32 and 0.18 ppm, respectively (see Figure S11).

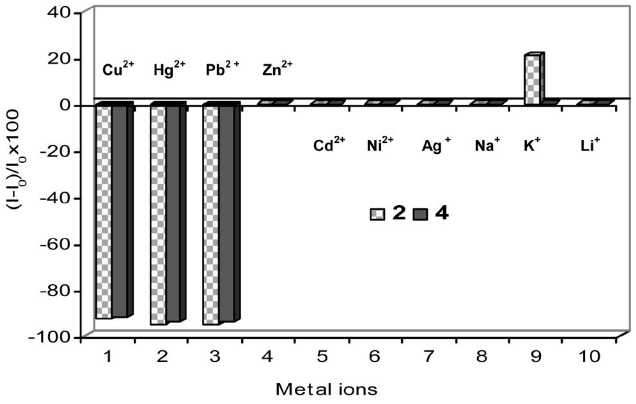


Figure 2. Changes in the fluorescence intensity [$(I - I_0)/I_0 \times 100$] of receptor **2** and **4** (each at 2.5 μM) in $MeCN/CH_2Cl_2$ (1:1) upon addition of 100 equiv. of various metal perchlorates. Excitation wavelength: 343 nm. I_0 is the fluorescence intensity at 490 nm of each free host and I is the fluorescence intensity after the addition of metal ions.

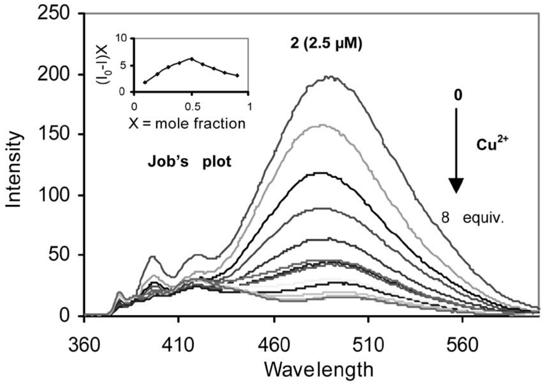


Figure 3. Changes in fluorescence emission spectra of **2** upon addition of Cu^{2+} ions in $MeCN/CH_2Cl_2$ (1:1; $\lambda_{\text{excitation}}$ = 343 nm). Inset: Job's plot showing a 1:1 stoichiometry.

Fitting the changes in the fluorescence spectra of compound **2** with K^+ ions in the non-linear regression analysis program SPECFIT gave a good fit and demonstrated that a 1:1 stoichiometry of the host and guest was the most stable species in solution with a binding constant ($\log\beta_1$) of 2.90. Selective K^+-binding by the crown-5 ring of **2** was also proved by an experiment in which K^+ was titrated against the **2**·Cu^{2+} complex (see below). The increase in the fluorescence was supported by the quantum yield,[32] which increased from $\phi_f = 0.49$ to 0.60 in dry THF. As compound **2** contains two different metal-ion binding sites, a metal ion will choose the more favourable one when added to a solution of **2**. The two nitrogen atoms of the imines prefer to bind Cu^{2+}, Pb^{2+} and Hg^{2+}, which results in fluorescence quenching, whereas the crown-5 ring binds the K^+ ion, which results in a small fluorescence enhancement.

We observed an interesting on–off switching process relating to cation exchange based upon discrimination between K^+ and Cu^{2+} ions (Figure 4). When K^+ was added to a solution of the **2**·Cu^{2+} complex the fluorescence intensities of both the excimer and monomer bands gradually increased and reached a plateau after the addition of about 698 equiv. of K^+ ions to the **2**·Cu^{2+} complex (Figure 5). However, the typical shape and full intensity of the excimer emission band could not be obtained on addition of K^+ ions to the **2**·Cu^{2+} complex, which may be a result of less overlapping of the pyrene dimer and thus a less effective HOMO–LUMO interaction in the excited state.[26] The revived fluorescence intensity on addition of K^+ ions is attributed to a negative heterotropic allosteric effect.[24] Earlier Budka et al. reported such a negative allosteric effect between anions in urea derivatives of conventional calixarenes.[24c]

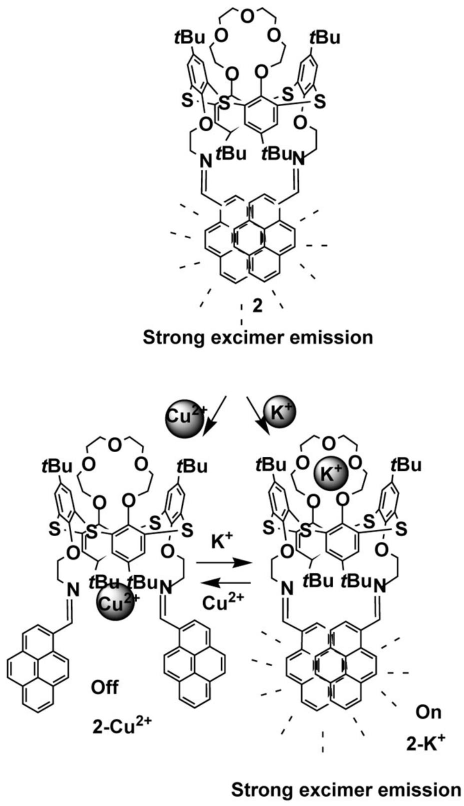


Figure 4. Receptor **2** showing allosteric behaviour with Cu^{2+} and K^+ ions.

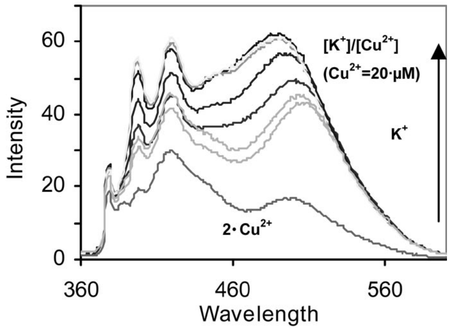


Figure 5. Fluorescence emission changes on addition of K^+ ions to a solution of the **2**·Cu^{2+} complex in $MeCN/CH_2Cl_2$ (1:1; $\lambda_{excitation}$ = 343 nm).

In the reverse of this metal-ion exchange process, when Cu^{2+} was gradually added to a solution of the **2**·K^+ complex, the fluorescence was again shown to be quenched by the Cu^{2+} (Figure 6), which shows that Cu^{2+} moves in and the K^+ moves out of **2**. On the other hand, the fluorescence intensity of the quenched complexes **2**·Hg^{2+} and **2**·Pb^{2+} could not be revived even after the addition of 1000 equiv. of K^+, which indicates that the complexation of K^+ to the crown ether site of **2** does not lead to a decomplexation of Hg^{2+} and Pb^{2+}. The reason for observing such allosteric behaviour with only Cu^{2+} and not with Hg^{2+} and Pb^{2+} is due to the fact that the complexation of Cu^{2+} to **2** is weak in comparison with the complexation of Pb^{2+} and Hg^{2+} to **2**, as is clear from the stability constant data (see above). We also carried experiments using Na^+ and Li^+ ions to affect the fluorescence of **2**·Cu^{2+}, but found that K^+ ions are the only effective cations to revive the fluorescence intensity. This suggests that the size of the crown ring is suitable only for the binding of K^+ ions. It was observed that the addition of K^+ liberates Cu^{2+} from the imino binding site of the **2**·Cu^{2+} complex more slowly than K^+ is released upon addition of Cu^{2+} to the **2**·K^+ complex. In the former the revival of the fluorescence continued to increase even after more than 500 equiv. of K^+ had been added. This suggests

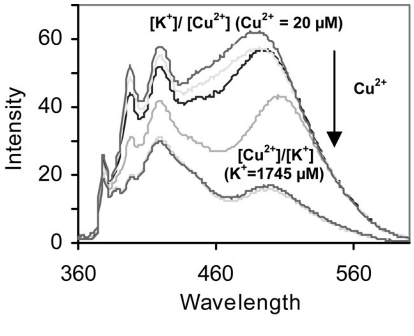


Figure 6. Fluorescence emission changes on addition of Cu^{2+} ions to a solution of **2**·Cu^{2+}·K^+ in $MeCN/CH_2Cl_2$ (1:1; $\lambda_{excitation}$ = 343 nm).

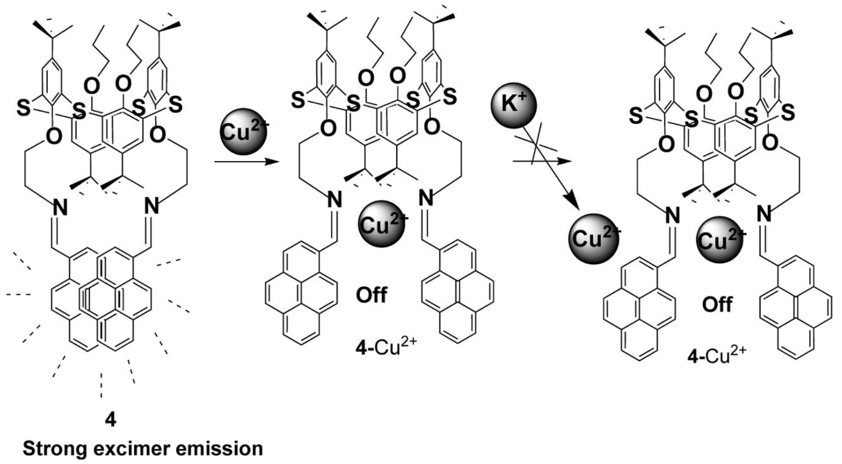


Figure 7. Receptor **4** showing no allosteric behaviour with Cu^{2+} and K^+ ions.

that Cu^{2+} is complexed by the imino nitrogen atoms stronger and faster than is K^+ by the polyether oxygen atoms.

On the other hand, the fluorescence intensity did not change when the same amount of K^+ was added to solutions of the **4**·Hg^{2+}, **4**·Pb^{2+} and **4**·Cu^{2+} complexes, which indicates that no cation exchange occurred as there is no binding site available for K^+ ions in receptor **4** (Figure 7).

Hence, the fluorescence intensity is not revived in the case of receptor **4**. This observation indicates that for "on–off" switching based on cation exchange the presence of more than one cation binding site is very important. The revival of fluorescence intensity could not be obtained when the experiment was carried out in THF/H_2O (95:5), which might be due to the hydration of K^+ ions by H_2O molecules.

Conclusions

We have synthesized a novel fluorescent chemosensor with two different cation binding sites on the lower rim of a thiacalix[4]arene framework with a 1,3-*alternate* conformation. In the free ligand, two pyrene moieties linked to cation recognition units composed of imine units form a strong excimer. The changes induced in the emission spectra by the addition of metal cations indicate that **2** responds to Hg^{2+}, Pb^{2+}, Cu^{2+} and K^+, whereas **4**, with propyl groups instead of a crown-5 ring, shows a response to Hg^{2+}, Pb^{2+} and Cu^{2+} ions. The fluorescence quenching of the monomer emission induced by Hg^{2+}, Pb^{2+} and Cu^{2+} in the case of both the receptors **2** and **4** can be ascribed to reverse PET and excimer quenching can be caused by the conformational change that occurs during the binding of these metal ions to the two nitrogen atoms. On the other hand, the addition of K^+ ions to a solution of **2** showed a small enhancement in emission intensity because K^+ is entrapped by the crown-5 unit. Interestingly, the fluorescence is quenched by Cu^{2+} but can be revived by the addition of excess K^+ ions to the **2**·Cu^{2+} complex. Thus, the metal-ion exchanges trigger an "on–off" switchable fluorescent chemosensor.

Experimental Section

General: All reagents were purchased from Aldrich and were used without further purification. MeCN was dried by heating at reflux with phosphorus pentoxide (P_2O_5) for 5 h and further treated with potassium carbonate for 2 h. HPLC grade dichloromethane was used to prepare a 1:1 mixture of MeCN/CH_2Cl_2. The fluorescence spectra were recorded with a Shimadzu RF 5301 PC spectrofluorimeter. ^1H and ^{13}C NMR spectra were recorded with a JEOL-FT NMR-AL 300 spectrometer using $CDCl_3$ or CD_3CN as the solvent and TMS as internal standards. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, d = doublet, br. = broad singlet, m = multiplet), coupling constants J [Hz], integration and interpretation. Silica gel 60 (60–120 mesh) was used for column chromatography. Solutions of compounds **2** and **4** and metal perchlorates were prepared in a mixture of MeCN/CH_2Cl_2 (1:1).

1,3-*alternate*-25,27-Bis(2-phthalimidoethoxy)thiacalix[4]crown-5 (1b): A mixture of **1a** (0.50 g, 0.47 mmol), Cs_2CO_3 (0.92 g, 2.82 mmol), tetraethylene glycol ditosylate (0.35 g, 0.71 mmol) in dry acetonitrile (100 mL) was heated at reflux for 48 h. After completion of the reaction the solvent was removed under reduced pressure to give a brown residue. Dichloromethane (50 mL) was added to the brown residue. The organic layer was washed three times with water (50 mL), dried with anhydrous sodium sulfate and distilled to give a brown solid, which was purified by chromatography on a silica gel column eluting with dichloromethane/hexane (1:1, v/v) to obtain **1b** in 50% yield (0.29 g) as a white solid; m.p. 210 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 [s, 18 H, $C(CH_3)_3$], 1.36 [s, 18 H, $C(CH_3)_3$], 3.00 (t, J = 8.1 Hz, 4 H, NCH_2), 3.36–3.39 (m, 8 H, OCH_2), 3.63 (br., 4 H, OCH_2), 3.95 (t, J = 7.5 Hz, 4 H, OCH_2), 4.05 (t, J = 9 Hz, 4 H, OCH_2), 7.38 (s, 4 H, Ar-H), 7.68 (s, 4 H, Ar-H), 7.80–7.83 (m, 8 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 31.43 (CH_3), 31.46 (CH_3), 34.37 (C), 55.97 (NCH_2), 66.36 (OCH_2), 70.13 (OCH_2), 71.41 (OCH_2), 73.54 (OCH_2), 116.73 (Ar-C), 117.17 (Ar-C), 118.10 (Ar-C), 121.88 (Ar-C), 126.36 (Ar-C), 126.88 (Ar-C), 127.69 (Ar-C), 127.94 (Ar-C), 145.39 (Ar-C), 146.91 (Ar-C), 151.12 (Ar-C), 165.65 (Ar-C) ppm. MS (FAB): m/z = 1226 $[M + 1]^+$. $C_{68}H_{76}N_2O_{11}S_4$ (1225): calcd. C 66.60, H 6.20, N 2.28; found C 66.40, H 6.28, N 2.29.

1,3-*alternate*-25,27-Bis(2-aminoethoxy)thiacalix[4]crown-5 (1c): A solution of compound **1b** (0.50 g, 0.41 mmol) and hydrazine monohydrate (0.41 g, 8.17 mmol) in ethanol (20 mL) was heated at reflux for 24 h and then cooled. During this time a solid separated. This was filtered, dissolved in chloroform and washed with 20% ammonium hydroxide solution. The chloroform layer was dried with anhydrous sodium sulfate and distilled under reduced pressure to give diamine **1c** in 80% yield (0.32 g) as a white solid; m.p. 280°C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.29 [s, 18 H, $C(CH_3)_3$], 1.37 [s, 18 H, $C(CH_3)_3$], 2.31 (t, *J* = 4.5 Hz, 4 H, NCH_2), 2.97 (t, *J* = 7.5 Hz, 4 H, OCH_2), 3.39 (br., 4 H, OCH_2), 3.62 (br., 4 H, OCH_2), 3.87–3.89 (m, 8 H, OCH_2), 7.29 (s, 4 H, Ar-H), 7.41 (s, 4 H, Ar-H) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 31.32 (CH_3), 31.41 (CH_3), 34.20 (C), 34.35 (C), 51.52 (NCH_2), 69.23 (OCH_2), 70.19 (OCH_2), 71.46 (OCH_2), 73.53 (OCH_2), 127.57 (Ar-C), 127.96 (Ar-C), 129.04 (Ar-C), 130.51 (Ar-C), 130.70 (Ar-C), 131.18 (Ar-C), 146.31 (Ar-C), 156.17 (Ar-C) ppm. MS (FAB): *m/z* = 966 [M + 1]$^+$. $C_{52}H_{72}N_2O_7S_4$ (965): calcd. C 64.70, H 7.47, N 2.90; found C 64.58, H 7.49, N 3.01.

1,3-*alternate*-25,27-Bis[2-(pyrenyl)iminoethoxy]thiacalix[4]crown-5 (2): A solution of 1-pyrenecarbaldehyde (0.048 g, 0.21 mmol) in ethanol (5 mL) was added to a solution of **1c** (0.10 g, 0.10 mmol) in a 1:1 mixture of chloroform and ethanol (20 mL). The mixture was heated at reflux for 24 h. The solvent was evaporated to leave a crude product, which was crystallized from $CHCl_3$/MeOH to give compound **2** in 70% yield (0.10 g); m.p. 260°C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.35 [s, 18 H, $C(CH_3)_3$], 1.39 [s, 18 H, $C(CH_3)_3$], 3.08 (t, *J* = 7.5 Hz, 4 H, NCH_2), 3.34 (t, *J* = 7.5 Hz, 4 H, OCH_2), 3.42 (br., 4 H, OCH_2), 3.64 (br., 4 H, OCH_2), 4.02 (t, *J* = 6.0 Hz, 4 H, OCH_2), 4.05 (t, *J* = 9.0 Hz, 4 H, OCH_2), 7.42 (s, 4 H, Ar-H), 7.55 (s, 4 H, Ar-H), 7.55–8.5 (m, 18 H, pyrene Ar-H), 9.16 (s, 2 H, HC=N) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 31.53 (CH_3), 34.40 (C), 34.50 (C), 60.41 (NCH_2), 65.60 (OCH_2), 67.09 (OCH_2), 70.29 (OCH_2), 73.57 (OCH_2), 121.95 (Ar-C), 124.76 (Ar-C), 125.64 (Ar-C), 125.85 (Ar-C), 126.15 (Ar-C), 127.34 (Ar-C), 127.83 (Ar-C), 127.93 (Ar-C), 128.35 (Ar-C), 128.52 (Ar-C), 129.71 (Ar-C), 130.99 (Ar-C), 146.44 (Ar-C), 156.64 (Ar-C), 160.36 (Ar-C) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1650 cm^{-1}. MS (FAB): *m/z* = 1390 [M + 1]$^+$. $C_{86}H_{88}N_2O_7S_4$ (1389): calcd. C 74.35, H 6.34, N 2.02; found C 74.24, H 6.35, N 2.07.

1,3-*alternate*-25,27-Bis[2-(pyrenylimino)ethoxy]-26,28-dipropoxythiacalix[4]arene (4): A solution of 1-pyrenecarbaldehyde (0.058 g, 0.25 mmol) in methanol (5 mL) was added to a solution of diamine **3** (0.10 g, 0.11 mmol) in a 1:1 mixture of chloroform and methanol (20 mL). The mixture was stirred for 24 h to separate a solid, which was filtered, washed and recrystallized from chloroform and methanol. The compound **4** was obtained in 74% yield (0.11 g) as a yellow solid; m.p. 260 °C. ^1H NMR ($CDCl_3$, 300 MHz): δ = 1.28 [s, 18 H, $C(CH_3)_3$], 1.37 [s, 18 H, $C(CH_3)_3$], 0.66 (t, *J* = 7.5 Hz, 6 H, CH_3), 0.96–1.10 (m, 4 H, CH_2), 3.45 (t, *J* = 7.5 Hz, 4 H, NCH_2), 3.90 (t, *J* = 7.5 Hz, 4 H, OCH_2), 4.41 (t, *J* = 6.0 Hz, 4 H, OCH_2), 7.37 (s, 4 H, Ar-H), 7.58 (s, 4 H, Ar-H), 7.62–8.64 (m, 18 H, pyrene Ar-H), δ = 9.23 (s, 2 H, HC=N) ppm. ^{13}C NMR ($CDCl_3$, 300 MHz): δ = 10.18 (CH_2), 22.18 (CH_3), 31.24 (CH_3), 31.58 (CH_3), 34.25 (C), 34.49 (C), 60.57 (NCH_2), 67.20 (OCH_2), 70.15 (OCH_2), 122.23 (Ar-C), 124.48 (Ar-C), 124.80 (Ar-C), 125.42 (Ar-C), 125.70 (Ar-C), 125.91 (Ar-C), 126.35 (Ar-C), 127.33 (Ar-C), 127.47 (Ar-C), 127.84 (Ar-C), 127.99 (Ar-C), 128.16 (Ar-C), 128.43 (Ar-C), 129.75 (Ar-C), 130.32 (Ar-C), 131.10 (Ar-C), 132.78 (Ar-C), 134.52 (Ar-C), 135.68 (Ar-C), 145.70 (Ar-C), 145.81 (Ar-C), 156.30 (Ar-C), 157.36 (Ar-C), 160.48 (Ar-C) ppm. IR (KBr): $\tilde{\nu}_{max}$ = 1635 cm^{-1}. MS (FAB): *m/z* = 1315 [M + 1]$^+$. $C_{84}H_{86}N_2O_4S_4$ (1314): calcd. C 76.70, H 6.54, N 2.13; found C 76.63, H 6.59, N 2.16.

Fluorescence Titrations: Fluorescence titrations were performed on 2.5×10^{-6} M solutions of ligands **2** and **4** in MeCN/CH_2Cl_2. Typically, aliquots of standard solutions (10^{-1} to 10^{-4} M) of freshly prepared $M(ClO_4)_2$ (M = Cu^{2+}, Hg^{2+}, Pb^{2+}, Zn^{2+}, Ni^{2+}, Cd^{2+}, Ag^+, K^+, Na^+ and Li^+) in MeCN/CH_2Cl_2 (1:1) were added and the fluorescence spectra of the samples recorded.

^{1}H NMR Experiments: The stock solution (10 mM) of receptor **2** was prepared in $CDCl_3$/CD_3CN (8:2). Similarly, stock solutions (20 mM) of perchlorate salts (K^+, Pb^{2+}, Hg^{2+}) were prepared in $CDCl_3$/CD_3CN (8:2).

Fluorescence Quantum Yield: The fluorescence quantum yield ϕ_f for **2** was determined at room temperature in analytical grade THF using optically matching solutions of resublimed pyrene (ϕ_f = 0.65) in ethanol as the standard at an excitation wavelength of 343 nm from a xenon lamp of the spectrofluorophotometer and the quantum yield was calculated by using Equation (1), in which ϕ_{fs} is the radiative quantum yield of the sample, ϕ_{fr} the radiative quantum yield of reference, A_s and A_r are the absorbances of the sample and the reference, respectively, D_s and D_r the areas of emission for the sample and reference, L_s and L_r are the lengths of the absorption cells, and N_s and N_r are the refractive indices of the sample and reference solutions (pure solvents were assumed).

$$\phi_{fs} = \phi_{fr} \times \frac{1-10^{-A_rL_r}}{1-10^{-A_sL_s}} \times \frac{N_s^2}{N_r^2} \times \frac{D_s}{D_r} \tag{1}$$

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data for compounds **1b**, **1c**, **2** and **4** including ^{1}H and ^{13}C NMR spectra and mass spectra, The ^{1}H NMR spectra of **2** in the presence of metal ions, UV/Vis and fluorescence emission spectra of **2** and **4**.

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