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A dipyrenyl calixazacrown chemosensor for Mg^{2+}

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ABSTRACT

A new fluorogenic calix[4]tetraaza-crown-6 (**4**) bearing two pyrene amide groups has been prepared. It was shown to be selective for Mg^{2+}. When Mg^{2+} is bound to **4**, the pyrene monomer emission increased while the excimer emission declined in a ratiometric manner. It is shown by ^1H NMR that this ratiometric change is due to the conformational changes of the pyrenes during the chelation of Mg^{2+} by the amide functions to form a 1:1 complex.

1. Introduction

Sensing of a metal ion with selective analytical reagents remains a challenge for environmental and biological applications.[1] With the advent of supramolecular chemistry, the design and synthesis of optically active chemical sensors for specific detection of metal ions has become a growing field of research.[2] A chemical sensor includes two components, a reporter unit, for example, a fluorophore, and an ionophore, which can be either independent species or covalently linked in one molecule and additionally a mechanism for communication between them.[3] When the analyte binds to the recognition center, changes occur in the optical properties (e.g., enhancement or inhibition of absorption or fluorescence) of the chemosensor. Fluorophores have recently found applications in self-assembled chemosensors,[4] for signal amplification by allosteric catalysis,[5] in supramolecular analytical chemistry,[6] and as fluorescent and photochromic chemosensors.[7]

Fluorescent chemosensors for cations composed of a cation recognition unit (ionophore) together with a fluorogenic unit (fluorophore) are usually described as fluoroionophores. An effective fluoroionophore must convert the cation recognition by the ionophore into an easily monitored and highly sensitive light signal from the fluorophore.[8] As fluorogenic units, pyrenes (Py) are one of the most useful tools due to their relatively efficient excimer formation and emission.[9] 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 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 the interaction of an excited pyrene (Py*) unit with a ground state pyrene (Py) unit.[10]

The choice of ionophore is crucial for the development of an effective sensor and many systems have been developed including a range of macrocycles. Since their characterization and isolation by Gutsche et al.[11] in the 1970s, the cyclooligomeric phenols known as calixarenes[12] have received much interest as basic molecular platforms for the construction of desired molecular architectures with desired properties.[13] More recently, calix[4]arenes have been incorporated into a large variety of fluorescent ion sensors.[14] For example, Broan reported a calixarene containing pyrenyl ester groups forming an intramolecular excimer due to strong π–π interaction between two pyrene units.[15] Similarly we recently described a pyrenyl-appended triazole-based calix[4]arene as a fluorescent sensor for Cd^{2+} and Zn^{2+}.[16]

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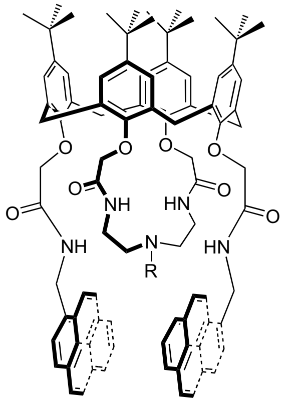
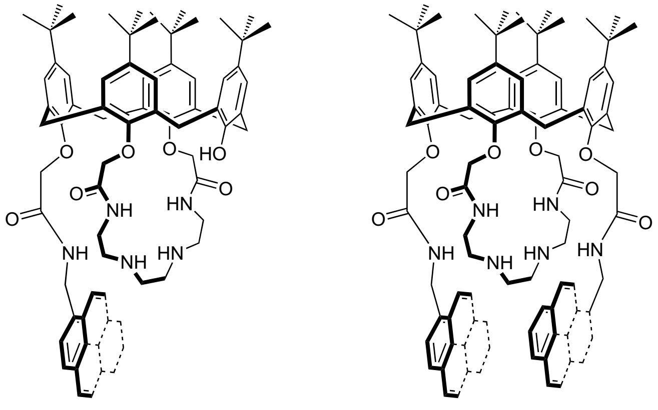


1 R = H **2** R = -$CH_2CH_2NH_2$

In precedent papers, we have described the synthesis and fluorescent properties of calix[4]arene chemosensors **1** and **2**.[17,18] The fluorogenic calix[4]triazacrown-5 (**1**), in cone conformation and bearing two pyrene amido groups, revealed an excimer emission at 448 nm when excited at 343 nm.[17] Binding properties of **1** were investigated toward metal ions (Li^+, Na^+, K^+, Cs^+, Pb^{2+}, Co^{2+}) in acetonitrile.[17] Among the metal ions tested, Pb^{2+} and Co^{2+}, known as quenching metal ions, quenched of the fluorescence of **1** both in monomer and particularly in the excimer.[17] This was attributed to a combination of heavy metal effect, reverse-PET, and conformational changes. NMR showed that Pb^{2+} is located in the triazacrown-5 with the turning of the amido carbonyl groups inside the azacrown loop to bind the metal.[17] In a subsequent paper, fluorogenic calix[4]arene (**2**) (corresponding to **1** in which a pendent ethylene amine (–$CH_2CH_2NH_2$) is attached on the central nitrogen atom of the triazacrown-5) has been prepared and displayed a relative weak emission due to a PET process between the NH_2 function and the fluorogenic pyrenes.[18] Addition of various metal ions (Li^+, Na^+, K^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Pb^{2+}, Zn^{2+}) to acetonitrile solutions of **2** reduced the PET due to interactions of NH_2 with the included metal ions.[18] As for **1**, Pb^{2+} was shown to be encapsulated in the azacrown loop with the carbonyl functions pointing inside the cavity and with the participation of the –$CH_2CH_2NH_2$ arm.[18] In contrast, both monomer and excimer emissions were observed to increase due to a CHEF effect and unchanged conformation with the other cations.[18]

The results observed for **1** and **2** led us to investigate fluorogenic cone calix[4]tetraaza-crown-6 (**4**) bearing two pyrene amido groups in which the crown loop is larger due to an additional –CH_2CH_2NH– unit (Fig. 1). The corresponding mono-pyrene derivative **3** was prepared for comparison. The selective sensing capability of **4** for magnesium over a wide range of competing cations with respect to ratiometric fluorescent signals is reported.[19]



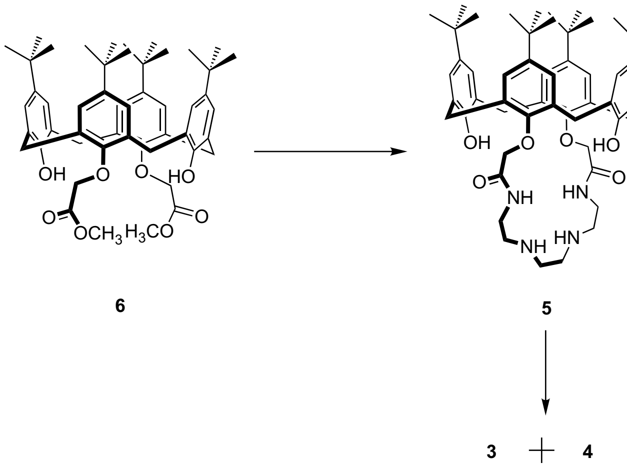
3

4

Figure 1. Structure of fluorescent sensors **3** and **4**.

2. Synthesis of calixazacrowns

The synthesis of both monopyrenyl **3** and dipyrenyl **4** derivatives necessitates the preparation of the precursor *p-tert*-butylcalix[4]tetraaza-crown-6 (**5**) (Scheme 1).



Scheme 1. Synthesis of **3–5**.

The chemistry of calixazacrowns has recently been reviewed and intermediate *p-tert*-butylcalix[4]tetraaza-crown-6 (**5**) was prepared by a procedure similar to those described for the preparation of calixazacrowns.[20] Thus, 1,3-dimetylester *p-tert*-butylcalix[4]arene (**6**)[21] was reacted with 4 equiv of commercial triethylenetetramine in 1:4 mixture of toluene/methanol with stirring for 6 days. It was obtained pure by precipitation with methanol. The introduction of the pyrene reporters was achieved through alkylation of **5** with 2.5 equiv of *N*-(1-pyrenemethyl)chloroacetamide (**7**)[22] with 1 equiv of K_2CO_3 as base and an excess of KI as catalyst with a 24 h-reflux in acetonitrile. Elution of the reaction residue on silica gel using 95:5 CH_2Cl_2/CH_3OH as eluent gave first dipyrenyl-*p-tert*-butylcalix[4]tetraaza-crown-6 (**4**) (R_f=0.45, 42% yield) in addition to the monopyrenyl-*p-tert*-butylcalix[4]tetraaza-crown-6 (**3**) (R_f=0.33, 21% yield). Calixarenes **3–5** were

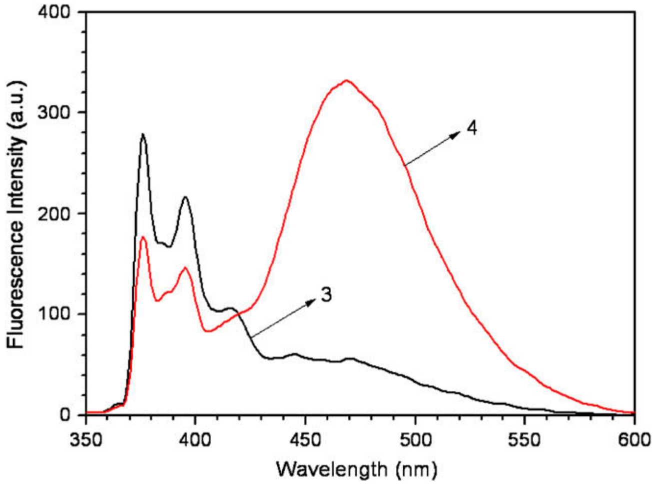


Figure 2. Fluorescence spectra of **3** and **4** (5.0 μM) in CH_3CN. The excitation wavelength is 340 nm.

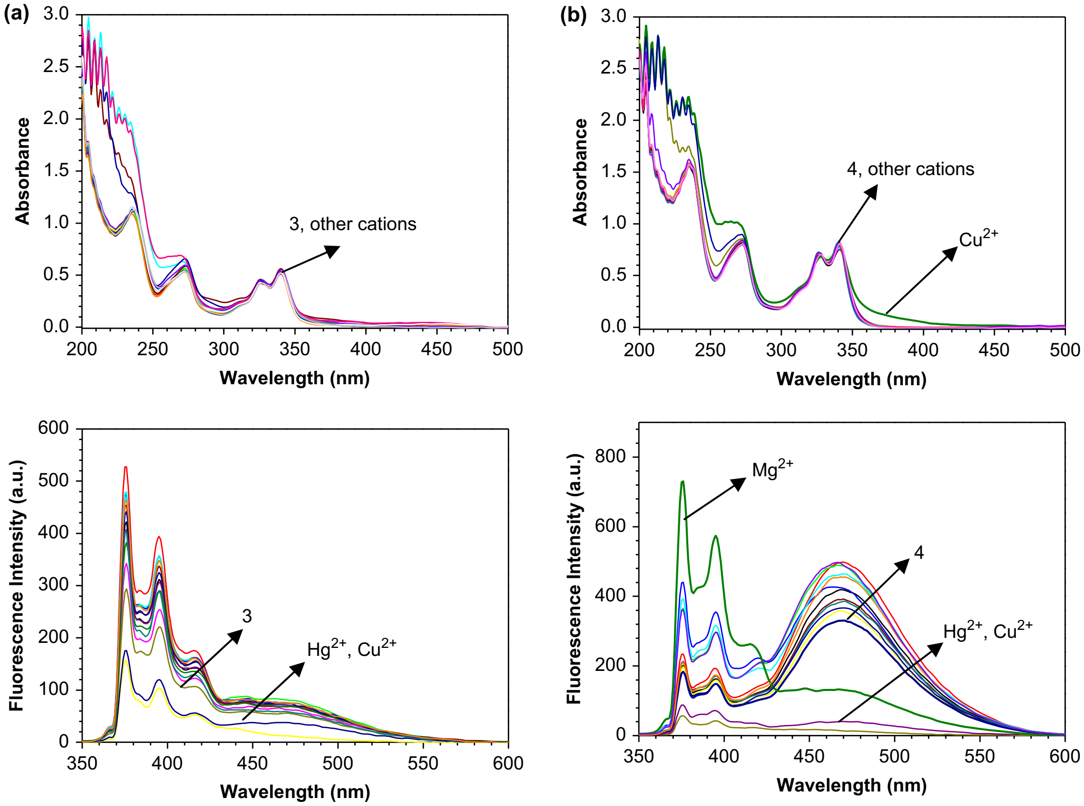


Figure 3. UV/vis and fluorescence spectra of (a) **3** and (b) **4** upon addition of ClO_4^- salt of Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, and Al^{3+} (50 equiv) in CH_3CN (UV: 20 μM, fluorescence: 5.0 μM).

fully characterized by ^1H NMR, MALDI-TOF mass spectrometry, and elemental analysis (Supplementary data, Figs. S1–S6). The conservation of the initial fixed cone conformation of the dimethyl ester calix[4]arene (**6**) was confirmed by the presence of doublets for the ArC*H*$_2$Ar protons at ∼3 and 4 ppm. The presence of the amido functions was deduced from the two distinct triplets at ∼7–9 ppm for the azacrown-CON***H*** and PyCH$_2$N***H***CO. The cone conformation of **5** was also confirmed by the determination of the crystal structure of its tetra-methanol solvate (Fig. S7).

3. Results and discussion

The optical properties of both **3** and **4** were investigated. On excitation at 340 nm, the maximum absorption wavelength of the pyrene of **4** displays both monomer and excimer emission at 375 and 468 nm, respectively, whereas in **3** a strong monomer emission is observed at 375 nm (Fig. 2). It is notable that the formation of the excimer emission in **4** is caused by an intramolecular interaction between Py and Py* where two pyrenes are likely to be in parallel.

The binding properties of **3** and **4** toward metal ions were investigated by monitoring the absorption and fluorescence changes upon addition of the perchlorate salt of a wide range of cations including Na^+, K^+, Rb^+, Cs^+, Ag^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, Pb^{2+}, and Al^{3+} in CH_3CN. The UV and fluorescence changes are depicted in Figure 3 and 4. Compounds **3** and **4** show two characteristic absorption bands centered at 326 and 340 nm for pyrene unit. No considerable band shift was observed in addition of other metal cations (50 equiv).

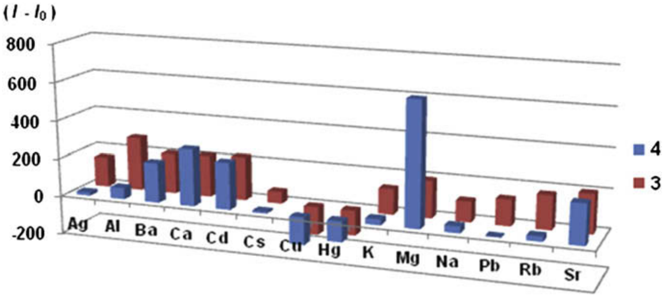


Figure 4. Fluorescence changes (I–I_0) of **3** and **4** upon the addition of various metal cations. Conditions: **3** and **4**, 5.0 μM in CH_3CN; excitation at 340 nm; emission at 375 nm; metal ions, 50 equiv in CH_3CN. I_0: fluorescence emission intensity of free **3** and **4**. I: fluorescence emission intensity of metal ion-complexed **3** and **4**.

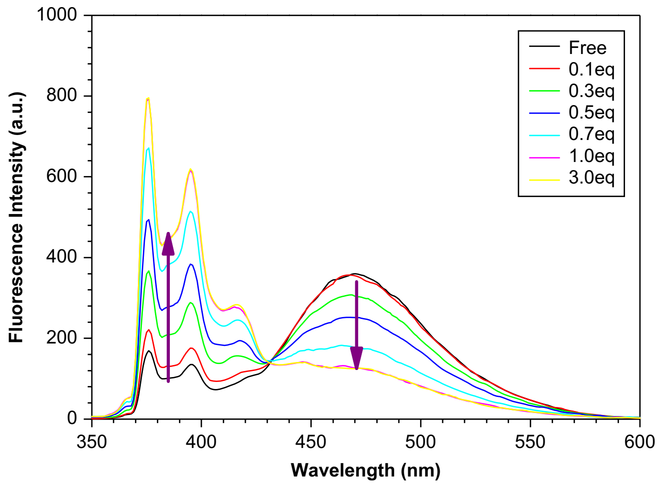


Figure 5. Fluorescence spectra of **4** (5.0 μM) in CH_3CN upon addition of increasing concentrations of $Mg(ClO_4)_2$ (0, 0.1, 0.3, 0.5, 0.7, 1.0, 3.0 equiv) with an excitation at 340 nm.

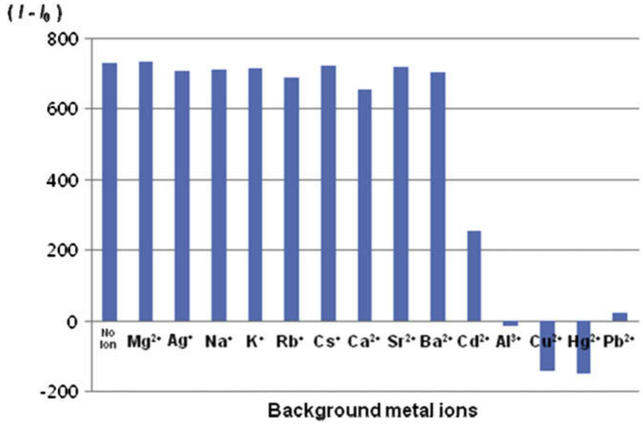


Figure 6. Fluorescent intensity of **4** (5.0 μM) upon addition of 10 equiv Mg^{2+} in the presence of 50 equiv of other metal ions in CH_3CN at 375 nm.

Addition of Mg^{2+} ion to the CH_3CN solution of **4** bearing two pyrene amido units induced a remarked ratiometry where the monomer emission increases while its excimer emission declines. It is supposed that the ratiometric change of **4** is due to conformational changes of the two pyrenyl moieties during Mg^{2+} complexation. In addition, we observed that when other heavy metal ions such as Hg^{2+} and Cu^{2+} were added to the solution of **4**, both monomer and excimer emissions were quenched because of the heavy metal ion effects. In contrast, **3** bearing only one pyrene amide unit shows a little enhanced monomer emission upon addition of Mg^{2+} ion and other metal ions.

Figure 5 shows the titration profile of **4** (5.0 μM) upon the addition of Mg^{2+} ion. When the concentration of Mg^{2+} is increased up to 5.0 μM, intensities of the monomer and excimer emissions increase and decreases by fourfold, respectively, at the same time. The association constant (K_a) of **4** was thus determined to be 1.17×10^6 M^{-1} for the Mg^{2+} ion. In Job plotting (Fig. S8), maximum fluorescence change was observed when the molar fraction of compound **4** versus Mg^{2+} is 0.5 indicative of a 1:1 complex **4**·$Mg(ClO_4)_2$.

To confirm **4** as an ion-selective fluorescence chemosensor for Mg^{2+} the effect of competing metal ions was determined. Compound **4** (5.0 μM) was treated with 10 equiv Mg^{2+} in the presence of other metal ions (50 equiv). As shown in Figure 6, no interference in detection of Mg^{2+} was observed in the presence of Ag^+, Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+} ions. However, the ratiometry of **4** is quite a bit interfered by the addition of Cu^{2+}, Hg^{2+}, Pb^{2+} ions because of the heavy metal ion effects. Thus it is notable that **4** can be at least used as a Mg^{2+} selective ratiometric fluorescent sensor in the presence of most of the alkali metal and alkaline earth metal cations.

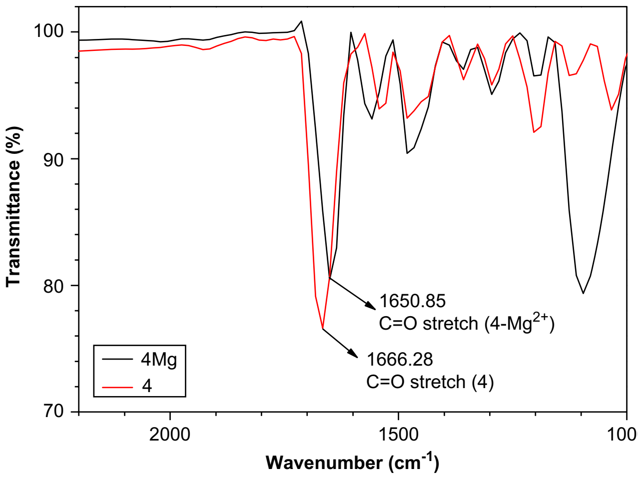


Figure 7. IR spectra of **4** and **4**-Mg^{2+}.

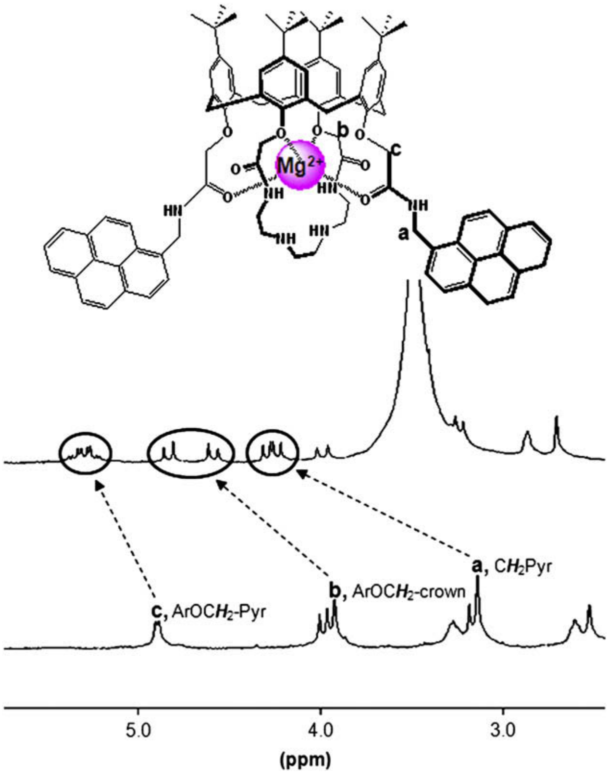


Figure 8. Partial ^1H NMR spectra of **4** in CD_3CN and in the presence of an excess of $Mg(ClO_4)_2$ (full spectra are available in Supplementary data, Figs. S9 and S10).

^1H NMR spectroscopy of **4** and **4**-Mg^{2+} in CD_3CN was undertaken to have more information on the structure of the complex formed during the fluorescence studies (Figs. S9 and S10). The spectrum of **4**-Mg^{2+} showed the whole molecular symmetry of the calixarene unit of **4** is maintained during complexation. Two singlets were observed at 1.08 and 1.14 ppm for the *tert*-butyl groups and an *AB* system at 3.29 and 3.98 ppm with J=6.0 Hz was observed for the $ArCH_2Ar$ macrocyclic protons of **4**-Mg^{2+} evidencing a cone conformation of the calixarenes. The main spectral differences are shown in Figure 8. One can see that methylene CH_2 singlets (a) and (b) and doublet (c) of **4** are splitted into a series of *AB* systems during complexation. All the protons involved are close to the CON*H* functions that chelates the metal through $C{=}O\cdots Mg^{2+}$.[23] The carbonyl–Mg^{2+} interaction was also detected by running IR spectrometry of free ligand **4** and its Mg^{2+}-complex in CH_3CN (see Fig. 7). One can observe a shift of the carbonyl band from 1666.28 cm^{-1} (free **4**) to 1650.85 cm^{-1} (**4**-Mg^{2+}).

In addition, the phenolic oxygen atoms may be involved in the binding events in agreement with hard-acid nature of Mg^{2+}. One can also assume the azacrown loop to act as a spacer to make the cavity big enough for accommodating Mg^{2+}. Similar results have been found for metal complexes of related **1** and **2**.[17,18] The appearance of these *AB* systems is assumed to be due to conformational changes of the azacrown loop during the accommodation process implying the methylene protons involved to become unequivalent.

CD_3CN solution of **4**-Mg^{2+} was directly submitted to mass spectrometry technique. Relevant peaks at m/z=1416.6064 and m/z=1439.5500 corresponding to the free ligand **4** and the 1:1

complex **4**·$Mg(ClO_4)_2$ complex, respectively, were observed (MALDI-TOF spectra of **4** and **4**-Mg^{2+} in CD_3CN made in the same conditions are given as Fig. S11).

4. Conclusions

In conclusion, new fluorogenic calix[4]tetraaza-crown-6 (**4**) bearing two pyrene amide groups has been prepared. It was shown to be selective for Mg^{2+}. When Mg^{2+} is bound to **4**, the pyrene monomer emission increased while the excimer emission declined in a ratiometric manner. This ratiometric change is due to the conformational changes of the pyrenes during the chelation of Mg^{2+} by the amide functions to form a 1:1 complex.

5. Experimental section

5.1. Preparation of 5

Dimethylester *p-tert*-butylcalix[4]arene (**6**) (0.800 g, 1.01 mmol), commercial triethylenetetramine (0.594 g, 4.04 mmol), and 1:4 toluene/methanol (40 mL) were stirred for 6 days at room temperature. The solvents were evaporated and the residue was precipitated with CH_3OH to give pure *p-tert*-butylcalix[4]tetraaza-crown-6 (**5**) as a white solid (0.657 g, 74%). Mp 238–239 °C. ^1H NMR (300 MHz, δ in ppm): 8.58 (t, J=5.0 Hz, 2H, CON***H***), 7.11 (s, 4H, Ar***H***), 6.69 (s, 4H, Ar***H***), 6.32 (s, 2H, ArO***H***), 4.50 (s, 4H, ArOC$\boldsymbol{H}_2$), 4.19 (d, J=14.0 Hz, 4H, AB system, ArC$\boldsymbol{H}_2$Ar), 3.53 (m, 4H, CONHC$\boldsymbol{H}_2$), 3.42 (d, J=14.0 Hz, 4H, AB system, ArC$\boldsymbol{H}_2$Ar), 2.94 (m, 4H, CONHCH$_2$C$\boldsymbol{H}_2$), 2.75 (s, 4H, CONHCH$_2$CH$_2$NHC$\boldsymbol{H}_2$), 1.31 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$), 0.88 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$). MW=875.25 calcd for $C_{54}H_{74}N_4O_6$. MALDI-TOF: m/z=875.61. Anal. Calcd: C, 74.10; H, 8.52. Found: C, 73.97; H, 8.61.

5.2. Preparation of 3 and 4

Calix[4]tetraaza-crown-6 (**5**) (0.250 g, 0.28 mmol), *N*-(1-pyrenemethyl)chloroacetamide (**7**) (0.211 g, 0.68 mmol), K_2CO_3 (0.040 g, 0.28 mmol), KI (excess), and CH_3CN (7 mL) were refluxed for 24 h. The solvent was evaporated and the residue portioned between 10% HCl and CH_2Cl_2. The organic layer was separated, dried over (Na_2SO_4), filtered, and the solvents evaporated. The residue was submitted to column chromatography on silica gel with 95:5 CH_2Cl_2/CH_3OH as eluent. Compound **4** (R_f=0.45, 0.170 g, 42%) was eluted first followed by **3** (R_f=0.33, 0.070 g, 21%).

5.3. Analytical data of 3

Yellowish solid. Mp 198–199 °C. ^1H NMR (300 MHz, δ in ppm): 8.99 (t, J=5.0 Hz, 1H, PyCH$_2$N***H***CO), 8.30–7.73 (m, 9H, Py***H***), 7.50 (t, J=5.0 Hz, 2H, CON***H***), 6.99 (s, 4H, Ar***H***), 6.70 (s, 2H, Ar***H***), 6.69 (s, 2H, Ar***H***), 6.64 (s, 2H, N***H***), 4.91 (d, J=5.0 Hz, 2H, PyC$\boldsymbol{H}_2$), 4.48 (s, 4H, ArOC$\boldsymbol{H}_2$-azacrown), 4.04 (d, J=14.0 Hz, 2H, AB system, ArC$\boldsymbol{H}_2$Ar), 4.02 (d, J=14.0 Hz, 2H, AB system, ArC$\boldsymbol{H}_2$Ar), 3.71 (m, 4H, CONHC$\boldsymbol{H}_2$), 3.10–3.30 (m, 10H, ArC$\boldsymbol{H}_2$Ar, ArOC$\boldsymbol{H}_2$-Py, CONHCH$_2$C$\boldsymbol{H}_2$), 2.79 (s, 4H, CONHCH$_2$CH$_2$NHC$\boldsymbol{H}_2$), 1.25 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$), 0.93 (s, 9H, C(C$\boldsymbol{H}_3$)$_3$), 0.88 (s, 9H, C(C$\boldsymbol{H}_3$)$_3$). MW=1146.53 calcd for $C_{73}H_{87}N_5O_7$. MALDI-TOF: m/z=1146.76. Anal. Calcd for $C_{73}H_{87}N_5O_7$: C, 76.47; H, 7.64. Found: C, 76.28; H, 7.61.

5.4. Analytical data of 4

Yellowish solid. Mp 214–215 °C. ^1H NMR (300 MHz, δ in ppm): 8.12–7.78 (m, 18H, Py***H***), 7.57 (t, J=5.0 Hz, 2H, PyCH$_2$N***H***CO), 7.31 (t, J=5.0 Hz, 2H, CON***H***), 6.97 (s, 4H, Ar***H***), 6.67 (s, 4H, Ar***H***), 6.65 (s, 2H, N***H***), 5.11 (d, J=5.0 Hz, 4H, PyC$\boldsymbol{H}_2$), 3.90 (s, 4H, ArOC$\boldsymbol{H}_2$-crown), 3.84 (d, J=14.0 Hz, 4H, AB system, ArC$\boldsymbol{H}_2$Ar), 3.22 (q, J=5.0 Hz, 4H, CONHC$\boldsymbol{H}_2$), 3.07 (d, J=14.0 Hz, 4H, AB system, ArC$\boldsymbol{H}_2$Ar), 2.99 (s, 4H, ArOC$\boldsymbol{H}_2$-Py), 2.50 (m, 4H, CONHCH$_2$C$\boldsymbol{H}_2$), 2.36 (s, 4H, CONHCH$_2$CH$_2$NHC$\boldsymbol{H}_2$), 1.28 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$), 0.92 (s, 18H, C(C$\boldsymbol{H}_3$)$_3$). MW=1417.85 calcd for $C_{92}H_{100}N_6O_8$. MALDI-TOF: m/z=1417.90. Anal. Calcd: C, 77.93; H, 7.10. Found: C, 78.03; H, 7.18.

5.5. Fluorescence studies

Fluorescence spectra were recorded with an RF-5301PC spectrophotometer. Stock solutions (1.00 mM) of the metal perchlorate salts were prepared in CH_3CN. Stock solutions of **3** and **4** (0.05 mM) were prepared in CH_3CN. For all measurements, excitation was at 340 nm with excitation and emission slit widths at 3.0 nm. Fluorescence titration experiments were performed using 5.0 μM solutions of **4** in CH_3CN and various concentrations of metal perchlorate in CH_3CN.

5.6. X-ray studies

X-ray data of **5** were collected at 100(2) K on a Nonius Kappa-CCD area detector diffractometer[24] using graphite-monochromated Mo Kα radiation and were processed with HKL2000.[25] The structure was solved by direct methods with SHELXS-97 and subsequent Fourier-difference synthesis and refined by full-matrix least-squares on F^2 with SHELXL-97.[26] No absorption correction was done. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms bound to oxygen and nitrogen atoms were found on a Fourier-difference map and those bound to carbon atoms were introduced at calculated positions; all were treated as riding atoms with an isotropic displacement parameter equal to 1.2 (OH, NH, CH, CH_2) or 1.5 (CH_3) times that of the parent atom.

5.6.1. *Crystal data for* **5**·*4CH$_3$OH*

$C_{58}H_{90}N_4O_{10}$, M=1003.34, monoclinic, space group $P2_1/c$, a=20.0233(9), b=13.8942(5), c=20.7549(8) Å, β=94.749(3)°, V=5754.4(4) Å^3, Z=4, μ(Mo Kα)=0.078 mm^{-1}, 173,600 measured reflections, 10,902 independent, 7772 with $I>2\sigma(I)$, R_{int}=0.032, 665 parameters, R_1=0.071, wR_2=0.211, S=1.017.

Acknowledgements

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Supplementary data

Supplementary data (NMR and cif file) associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.01.079.

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