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Synthesis and fluorescence sensing properties of novel pyrene-armed calix[4]arene derivatives

Ozlem Sahin, Mustafa Yilmaz *

Selcuk University, Department of Chemistry, Campus, 42031 Konya, Turkey

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Fluorogenic *tert*-butylcalix[4]arenes bearing two pyrene pendant groups at the lower rim were synthesized. Based on ratiometric changes of monomer and excimer emissions, the pyrene amine derivative of calix[4]arene has been found to act as a selective sensor for Pb^{2+} and Cu^{2+} ions, respectively, due to a conformational change upon chelation of these ions.

1. Introduction

Molecular recognition is a crucial process in biological systems, such as enzymes, antibodies or genes and is fundamental to supramolecular chemistry.[1–3] The design and the synthesis of fluorescent chemosensors for the detection of metal ions is an active and fascinating area of supramolecular chemistry.[4–8] Among chemosensory systems, the fluorescent method is very important due to its simpler instrumentation, high selectivity, and direct visual perception even in very dilute solutions.[9]

Fluorescent chemosensors for cations composed of a cation recognition unit (ionophore) together with a fluorogenic unit (fluorophore) are usually described as fluoroionophores.[10] The chemistry of calixarenes, cyclic oligomers composed of phenolic and methylene moieties, has been extensively studied in recent years. The preorganized binding sites, easy derivatization and flexible three dimensional steric structures make them perfect construction platforms for molecular design to generate fluorescent receptors.[11] Calix[4]arenes are important macrocyclic compounds and also ideal platforms for the development of complexing agents for metal ions.[12,13] Calixarenes substituted on the upper or lower rim may show selective cation recognition dependent on the cation ligating group. This group, known as the ionophore, may be a crown ether,[14] amide[15], Schiff base,[16,17] or other functional group. Recently, the cation–ionophore interaction has been monitored by a signaling moiety attached to the calixarene framework. The signaling moiety may be a fluorogenic unit, such as a pyrene, anthracene, naphthalene or dansyl group.[18] Broan reported that a calixarene-containing pyrenyl ester groups forms an intramolecular excimer due to strong π–π interaction between two pyrene units.[19]

Most calix[4]arene-based fluorescent sensors have been designed based on photophysical changes upon metal ion binding and their mechanisms include photoinduced electron transfer (PET),[20] photoinduced charge transfer (PCT),[21] formation of monomer/excimer,[22] and energy transfer.[23,24]

A few transition-metal cations, e.g., Cu^{2+}, Ni^{2+}, etc. have also been investigated. However, the generation of fluorescent sensors for transition metals is of increasing importance for biological and environmental applications. Unlike alkali and alkaline earth metals, transition metals do not differ too much in size, but they can establish coordinative interactions of very different energies, which can be used for discriminative purposes, especially for fluorescent sensing.[9]

Heavy metal cations, such as Cu^{2+} and Zn^{2+} ions are widely considered as pollutants as well as essential trace elements in biological systems.[25] Recently, the presence of heavy metal ions, such as Pb^{2+} in the environment at elevated level causes health related problems like anaemia, kidney damage, a disorder of the blood, memory loss, muscle paralysis and mental retardation by lead poisoning.[26] The development of chemosensors for soft transition-metal ions particularly needs attention because of

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* Corresponding author. Tel.: +90 332 2233873; fax: +90 332 2410520; e-mail address: myilmaz42@yahoo.com (M. Yilmaz).

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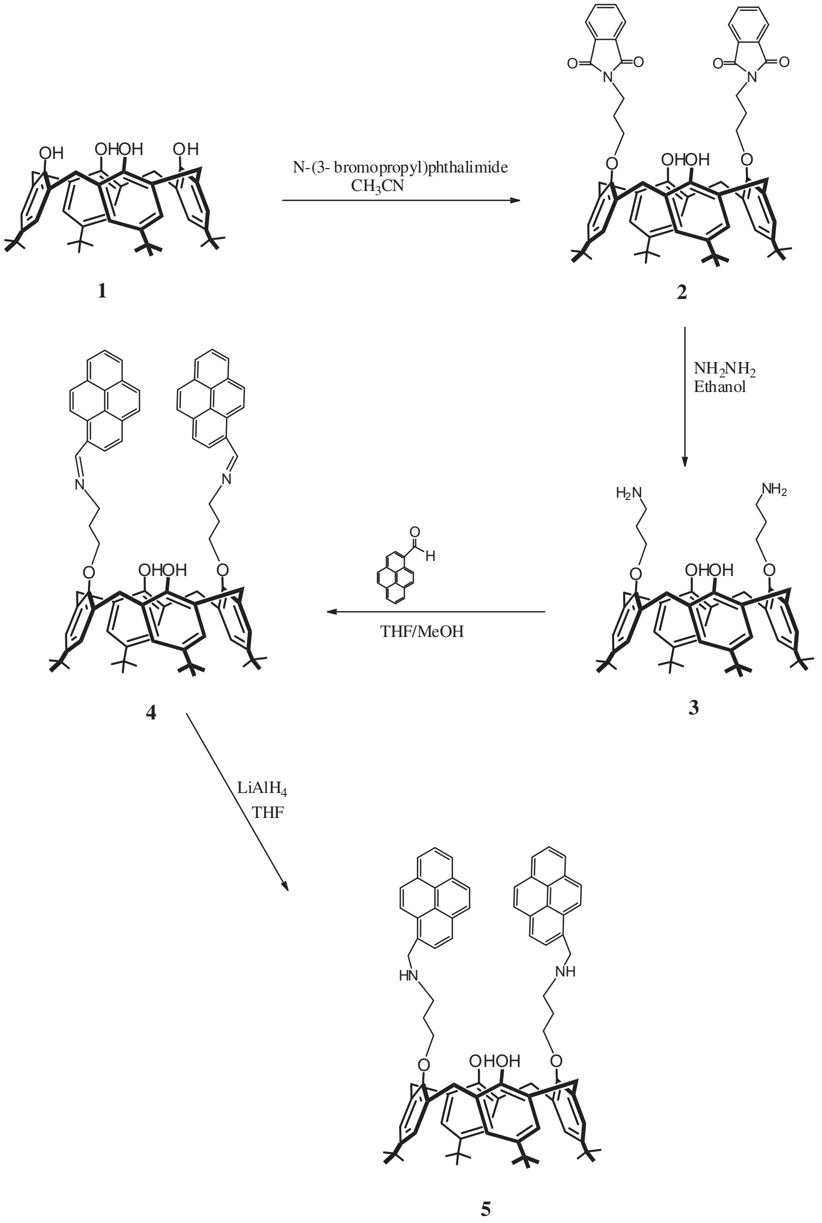
their toxic impact on our environments.[27] Among the soft metal ions, copper is the third most abundant essential heavy metal ion (after Fe^{2+} and Zn^{2+}) present in the human body. It plays an important role in fundamental physiological processes in organisms ranging from bacteria to mammals.[28] However, copper can be toxic if the level exceeds cellular needs. It is also capable of displacing other metals, which act as co-factors in enzyme-catalyzed reactions.[29,30]

Recently Kumar et al. reported[26] fluorescent detection of Pb^{2+} ions using *N*-(pyrenyl-1-methylimine) derivatized calix[4]arene. However, to the best of our knowledge, fluorescent signaling of lead (II) and cupper(II) using calix[4]arene derivatives possessing a pyrene amine moiety has not been reported up to now. We report herein the synthesis and fluorescent properties of fluorogenic *N*-(pyrenyl-1-methylimine) derivatized calix[4]arene (**4**–**5**), and binding properties of **5** towards metal ions ($Ca^{2+,}$ Cu^{2+}, Li^{+}, Mg^{2+}, Ba^{2+}, Na^{+}, Ni^{2+}, Pb^{2+} and Zn^{2+}) in acetonitrile/dichloromethane were investigated.

2. Results and discussion

2.1. Synthetic routes

The preparation of receptors **4** and **5** is depicted in Scheme 1. First, *tert*-butylcalix[4]arene **1**[31] was reacted with 3-bromopropyl phthalimide in the presence of K_2CO_3 to give bis(3-phthalimidopropoxy) calix[4]arene **2**.[32,33] The phthalimido groups were removed with hydrazine hydrate in EtOH to give bis(3-aminopropoxy)calix[4]arene **3**.[34,35] Bis(3-aminopropoxy)calix[4]arene **3** was reacted 1-pyrene carboxaldehyde to give receptor **4** in 70% yield. Finally, compound **5** was synthesized by reduction of **4** with $LiAlH_4$ in THF 66% yield. The structures of **4** and **5** were confirmed from their spectroscopic and analytical data. The IR spectra of compound **4** showed a stretching band 1627 cm^{-1} belong to CH=N groups. The formation of the diamine derivative of *p-tert*-butylcalix[4]arene (**5**) was confirmed by the disappearance of the characteristic CH=N bands of **4** at about 1627 cm^{-1} in the IR spectra.



Scheme 1. Synthesis of receptors **4** and **5**.

In general, the ^{1}H NMR spectra of compounds **4** and **5** showed two singlets (18H each) for *tert*-butyl protons, two singlets (4H each) for aromatic protons, one multiplet (18H each) for pyrene protons, one singlet (2H) for the imino protons of compound **4**and one singlet (2H) for the ArH$_{pyr}$ CH_2NH protons of **5**. As indicated by the ^{1}H NMR spectra, calixarenes **4** and **5** have a cone conformation. A typical AB pattern was observed for the methylene bridge ArCH$_2$Ar protons at 3.37 and 4.49 ppm (J=13 Hz) for **4**, 3.29 and 4.25 ppm (J=13 Hz) for **5** in ^{1}H NMR. The high field doublets at 3.37 ppm for **4** and 3.29 ppm for **5** were assigned to the equatorial protons of the methylene groups, whereas the low field signals at 4.49 ppm for **4** and 4.25 ppm for **5** were assigned to the axial protons.

2.2. Absorption spectra

The cation binding properties of compounds **4** and **5** were investigated by UV–vis and fluorescence spectroscopy. The titration experiments were carried out in CH_2Cl_2/CH_3CN (1:1 v/v) by adding aliquots of different metal ions. The UV–vis absorption spectra of the compounds **4** and **5** exhibit typical pyrene absorption bands at 350 nm for compound **4** (Fig. 1) and at 329 nm and 344 nm for compound **5** (Fig. 2). The addition of Zn^{2+}, Pb^{2+}, Mg^{2+} and Cu^{2+} ions (10 equiv) to a solution of **4**, the new absorption peak appeared at longer wavelength at 453 nm. Upon addition of Cu^{2+} and Pb^{2+} ions (10 equiv) to a solution of **5**, the new absorption peak appeared at longer wavelength at 451 nm. The colour of the solution of **4** and **5** changed from colourless to yellow in presence of Cu^{2+}, Zn^{2+}, Pb^{2+}, Mg^{2+} and Cu^{2+} ions. There was no change in the UV–vis spectra of the receptors **4** and **5** upon addition of metal ions Ca^{2+}, Li^+, Ba^{2+}, Na^+ and Ni^{2+}.

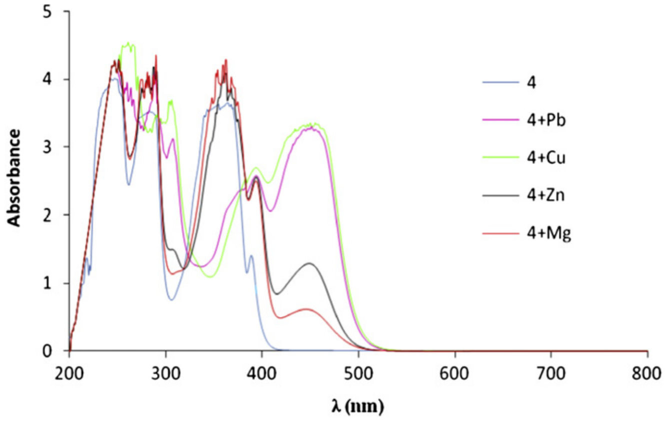


Fig. 1. UV–vis. spectra of **4** (1.10^{-4} M) upon addition of ClO_4^- salt of Zn^{2+}, Pb^{2+}, Mg^{2+} and Cu^{2+} (10 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

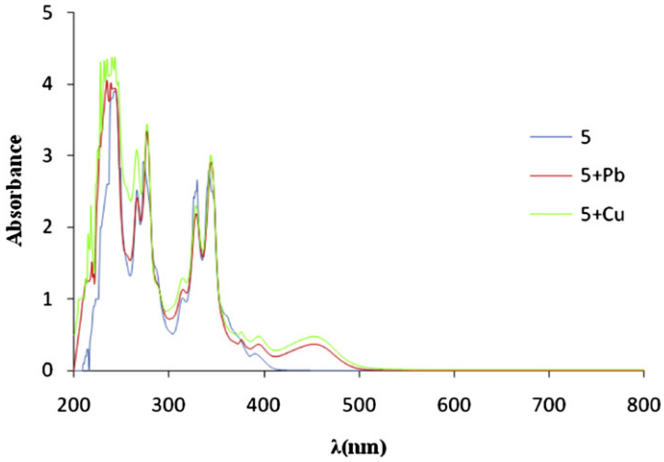


Fig. 2. UV–vis. spectra of **5** (1.10^{-4} M) upon addition of ClO_4^- salt of Pb^{2+} and Cu^{2+} (10 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

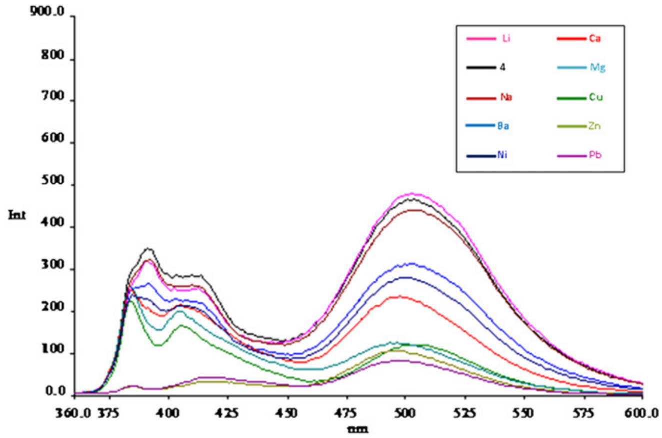


Fig. 3. Fluorescence spectra of **4** (1.10^{-6} M) upon addition of ClO_4^- salt of Ca^{2+}, Cu^{2+}, Li^+, Mg^{2+}, Ba^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} (10 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

2.3. Fluorescence spectra

The fluorescence spectrum of compound **4** gave a dual emission resulting from a pyrene monomer in the range of 370–450 nm and excimer at 503 nm by excitation of the pyrene moiety of **4** at 350 nm (Fig. 3). Upon addition of Pb^{2+} and Zn^{2+} ions (0–10 equiv) to the solution of compound **4**, a significant quenching in the fluorescence emission, which was attributed to **4**/Pb^{2+} and **4**/Zn^{2+} complexes were observed. The fluorescence titration profiles of **4** with Pb^{2+} and Zn^{2+} ions showed monomer and excimer quenching upon addition of 10.0 equiv of Pb^2 and Zn^{2+} ions (Fig. 4). Under the same conditions as used above for Pb^{2+} and Zn^{2+}, we also tested the fluorescence response of **4** to other metal ions such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+} Cu^{2+} besides Pb^{2+} and Zn^{2+}, as shown in Fig. 7, some fluorescence change of **4** occurred in the presence (10 equiv) of these metal ions. This remarkable fluorescence quenching induced by Pb^{2+} and Zn^{2+} is ascribed to reverse-PET from pyrene units to the nitrogen atom of which the electron density is diminished by metal complexation.[30] The quenching phenomenon was attributed to a combination of heavy metal ion effect, reverse-PET (photoinduced electron transfer) and conformational changes.

As shown in Scheme 1, compound **5** showed a typical monomer in the range of 360–410 nm and excimer at 460 nm, which was considerably quenched in the presence of Cu^{2+} and Pb^{2+}. When the concentration of Cu^{2+} and Pb^{2+} ions was increased up to 1.10^{-5} mol L^{-1} (10 equiv), more than 60% quenching of the initial fluorescence of **5** was observed (Fig. 5). However, when similar tests were carried out with other metal ions, such as Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+} and Zn^{2+}, only a minimal quenching has been observed (Fig. 8).

The fluorescence intensity of **5** in the presence of increasing amounts of Cu^{2+} and Pb^{2+} was shown in Fig. 6. The fluorescence intensity of the monomer and excimer emission at 460 nm of **5** gradually decreased with the increasing Cu^{2+} and Pb^{2+} concentrations (0–10 equiv). When Cu^{2+} and Pb^{2+} ions were added to compound **5**, the fluorescence intensity decreased because of the reverse-PET from the pyrene unit to the nitrogen atom caused by Cu^{2+} and Pb^{2+} ion binding as well as the heavy metal effect.

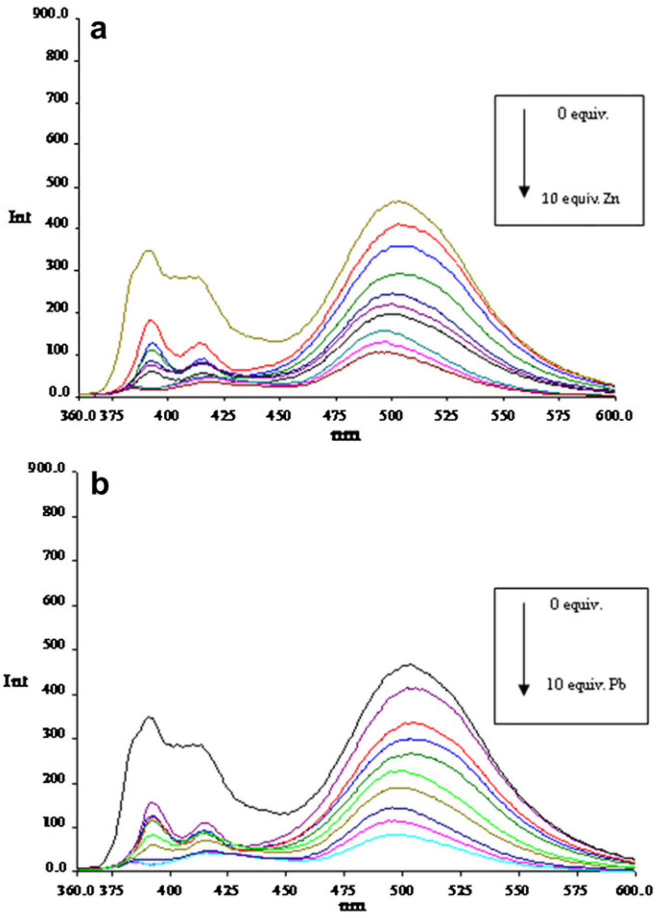


Fig. 4. Fluorescence spectra of **4** (1.10^{-6} M) in CH_2Cl_2/CH_3CN (1:1, v/v) upon addition of increasing concentrations of (a) $Zn(ClO_4)_2$ and (b) $Pb(ClO_4)_2$ (0–10 equiv) with an excitation at 350 nm.

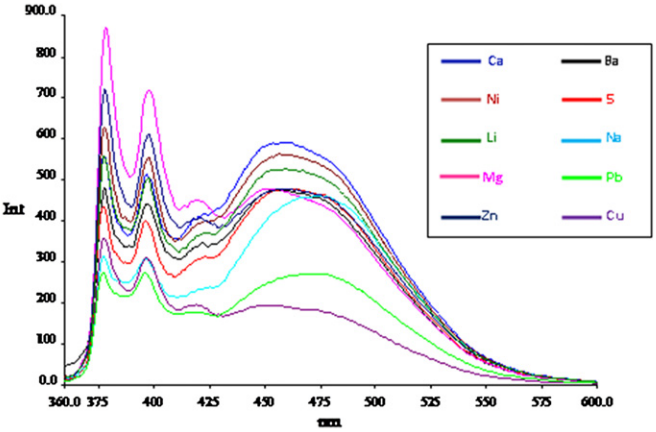


Fig. 5. Fluorescence spectra of **5** (1.10^{-6} M) upon addition of ClO_{4-} salt of Ca^{2+}, Cu^{2+}, Li^+, Mg^{2+}, Ba^{2+}, Na^+, Ni^{2+}, Pb^{2+} and Zn^{2+} (10 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

To confirm **5** as an ion-selective fluorescence chemosensor for Pb^{2+} the effect of competing metal ions was determined. Compound **5** (1.10^{-6} M) was treated with 10 equiv Pb^{2+} in the presence of other metal ions (100 equiv). As shown in Fig. 9, no interference in the detection of Pb^{2+} was observed in the presence of Li^+, Na^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Ni^{2+} and Zn^{2+}.

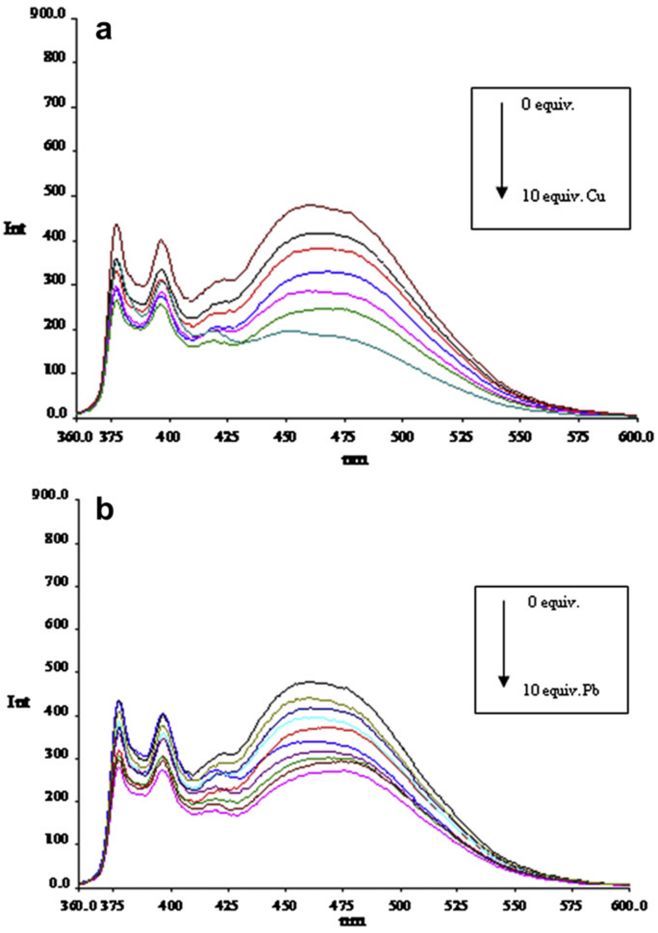


Fig. 6. Fluorescence spectra of **5** (1.10^{-6}) in CH_2Cl_2/CH_3CN (1:1, v/v) upon addition of increasing concentrations of (a) $Cu(ClO_4)_2$ and (b) $Pb(ClO_4)_2$ (0–10 equiv) with an excitation at 348 nm.

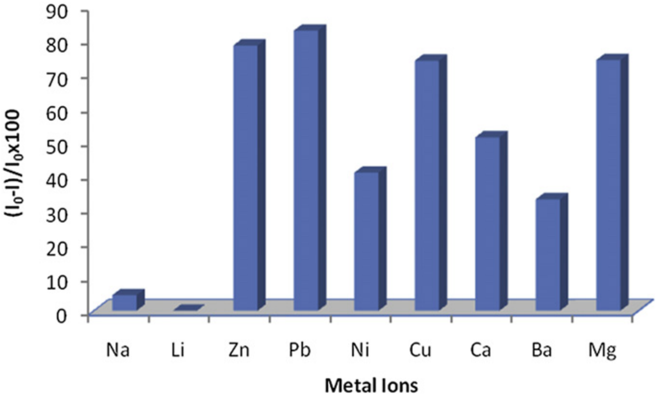


Fig. 7. Fluorescence quenching ratio $[(I_0-I/I_0)\times100]$ of **4** (1.0×10^{-6} M) at 503 nm upon addition of different metal ions (10.0 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

2.4. Determination of complex stoichiometry

In order to determine the stoichiometry of the **5**/Pb^{2+} and **5**/Cu^{2+} complex, the method of continuous variation (Job's plot) was also used. The total concentration of the compound **5** and Cu^{2+}, **5** and Pb^{2+} were constant (1×10^{-3} M), with a continuous variable molar fraction of guests ($[Cu^{2+}]/[\mathbf{5}]+[Cu^{2+}]$) and ($[Pb^{2+}]/[\mathbf{5}]+[Pb^{2+}]$). Fig. 10 shows the Job plot of compound **5** with Cu^{2+} and Pb^{2+} ions. The **5**/Cu^{2+} and **5**/Pb^{2+} complex concentration

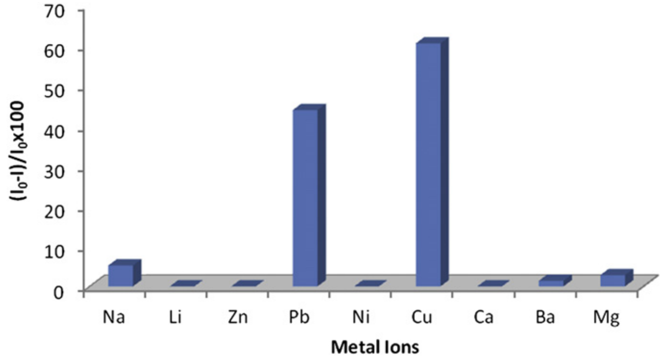


Fig. 8. Fluorescence quenching ratio [$(I_0-I/I_0)\times100$] of **5** (1.0×10^{-6} M) at 503 nm upon addition of different metal ions (10.0 equiv) in CH_2Cl_2/CH_3CN (1:1, v/v).

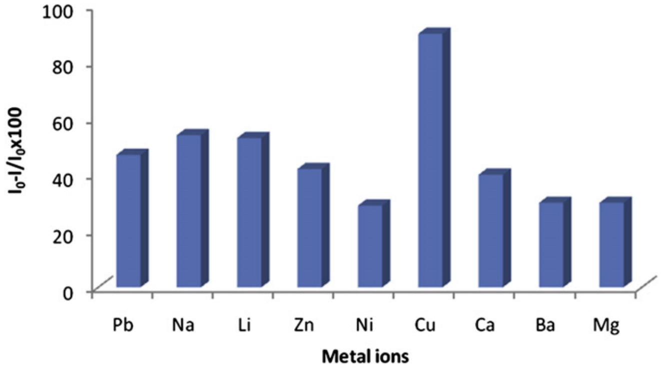


Fig. 9. Fluorescence quenching ratio [$(I_0-I/I_0)\times100$] of **5** (1×10^{-6} M) towards Pb^{2+} ions (10.0 equiv) in the presence of other metal ions (100.0 equiv, Ca^{2+}, Cu^{2+}, Li^+, Mg^{2+}, Ba^{2+}, Na^+, Ni^{2+} and Zn^{2+} in CH_2Cl_2/CH_3CN (1:1, v/v)).

approaches a maximum when the molar fraction of Cu^{2+} and Pb^{2+} are 0.5, which means **5** with Cu^{2+} and Pb^{2+} formed1:1 complexes (Fig. 10).

2.5. Stern–Volmer analysis

Stern–Volmer analysis was utilized to probe the nature of the quenching process in the complexation of Cu^{2+} and Pb^{2+}. Stern–Volmer plots are a useful method of presenting data on emission quenching. Plotting relative emission intensities (I_0/I) against quencher concentration [M] yields a linear Stern–Volmer plot for a static quenching process. Expressed as Eq. 1, the slope of this line is Ksv, the static quenching constant. I and I_0 are fluorescence intensities in the presence and in the absence of added metal cations.[36]

$$I_0/I = 1 + \mathrm{Ksv}[\mathrm{M}] \tag{1}$$

Fig. 11 shows the steady-state emission Stern–Volmer analysis for complexation of Zn^{2+} and Pb^{2+} by **4**, Cu^{2+} and Pb^{2+} by **5**. For both **4** and **5**, linear behaviour was observed for complexation of Cu^{2+}, Zn^{2+} and Pb^{2+}. These results are consistent with static quenching. The static quenching constants (Ksv) are given in the Table 1.

2.6. Determination of stability constants

The complex stability constant (β) was calculated using Valuer's method.[37] Accordingly the quantity $I_0/(I_0-I)$ is plotted versus [metal ion]$^{-1}$ with the stability constant given by the ratio of intercept/slope[18,38](Fig. 12).

The stability constants for complexation of Cu^{2+}, Zn^{2+} and Pb^{2+} with the two ligands was determined by fluorimetric titration. The

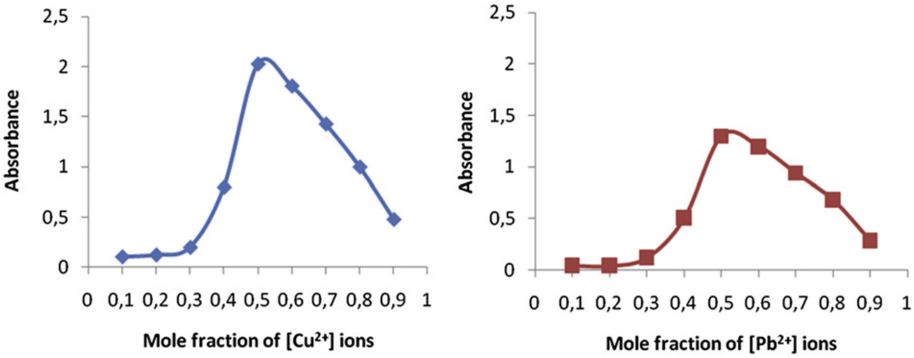


Fig. 10. Job's plot for compounds **5**, Pb^{2+} and Cu^{2+} ions, [**5**]+[Pb^{2+}] and [**5**]+[Cu^{2+}]=1×10^{-3} M in CH_3CN/CH_2Cl_2 (1:1, v/v).

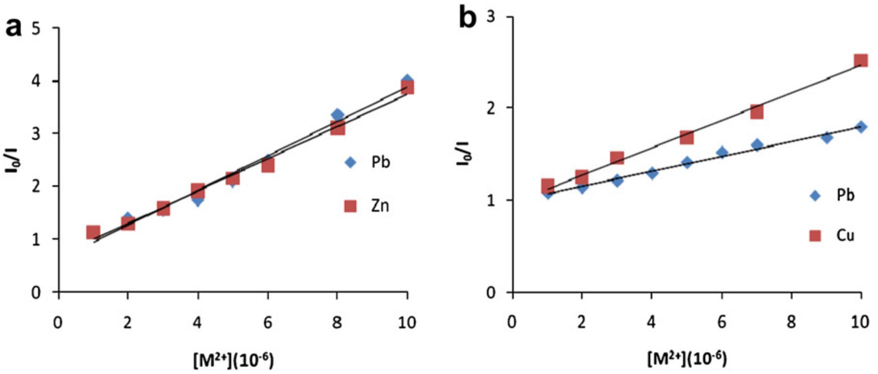


Fig. 11. Stern–Volmer plot for the fluorescence quenching of (a) Zn^{2+} and Pb^{2+} by 4, (b) Cu^{2+} and Pb^{2+} by **5** in CH_3CN/CH_2Cl_2 (1:1, v/v).

Table 1
Quenching constant for complexation of Zn^{2+} and Pb^{2+} by **4**, Cu^{2+} and Pb^{2+} by **5** in CH_3CN/CH_2Cl_2 (1:1, v/v) obtained from Fig. 11

Ligand		Static quenching constant (Ksv)	R^2
4	Zn^{2+}	$3.15\times10^5\pm0.04$	0.9823
	Pb^{2+}	$3.15\times10^4\pm0.01$	0.9823
5	Cu^{2+}	$1.49\times10^4\pm0.01$	0.9934
	Pb^{2+}	$8.15\times10^3\pm0.01$	0.9896

titration experiments were performed by adding solutions with various concentrations of metal perchlorate in CH_3CN/CH_2Cl_2 to solutions of the ionized ligand in the same solvent. The ligand concentration was held constant at 1×10^{-6} M.

Table 2 presents calculated stability constants for complexation of **4** and **5** with Cu^{2+}, Zn^{2+} and Pb^{2+}. Stability constants for complexation of **4** with Zn^{2+}, Pb^{2+} and **5** with Cu^{2+}, Pb^{2+} are approximately the same.

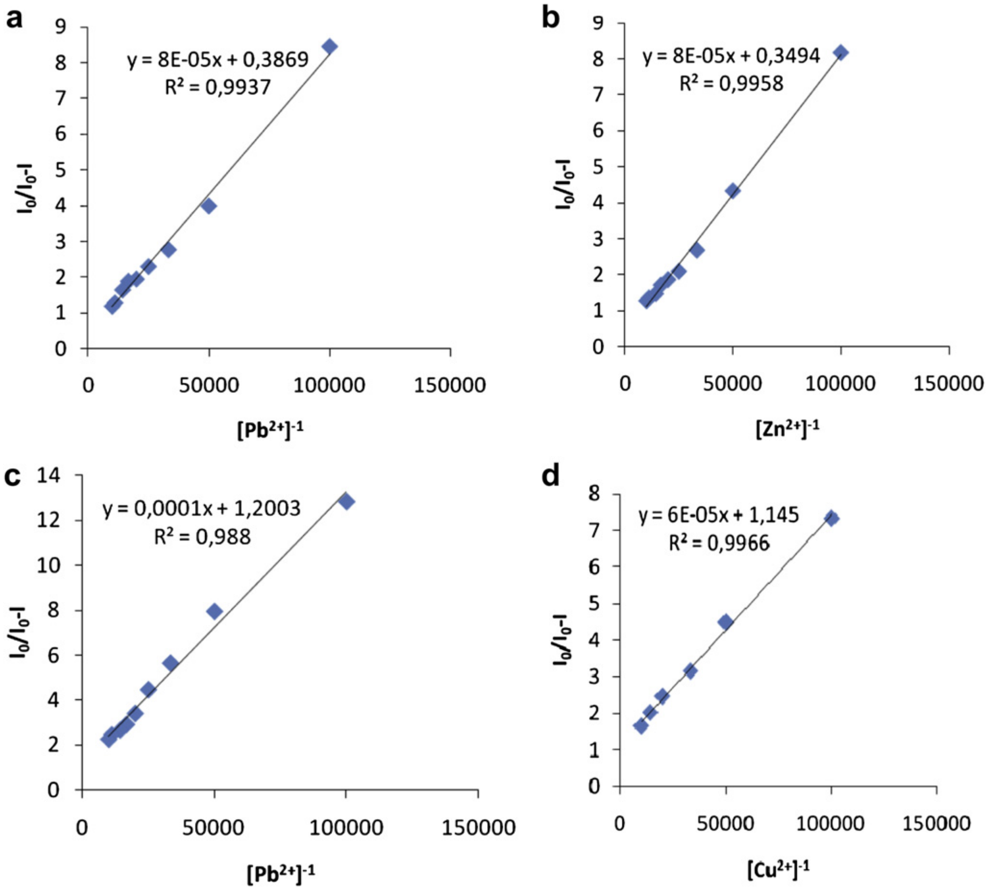


Fig. 12. Plot of $I_0/(I_0-I)$ versus $[M^{2+}]^{-1}$ for the spectrofluorimetric titration of (a) **4** with Pb^{2+}, (b) **4** with Zn^{2+}, (c) **5** with Pb^{2+}, (d) 5 with Cu^{+2} in CH_3CN/CH_2Cl_2 (1:1, v/v).

Table 2
Stability constants for complexation of Zn^{2+} and Pb^{2+} by **4**, Cu^{2+} and Pb^{2+} by **5** CH_3CN/CH_2Cl_2 (1:1, v/v) obtained from Fig. 12

Ligand	Cation	Stability constants (log β) $(M)^{-1}$
4	Zn^{2+}	3.64±0.10
	Pb^{2+}	3.68±0.20
5	Cu^{2+}	4.28±0.10
	Pb^{2+}	4.08±0.10

2.7. Analysis of ^1H NMR spectrum of complex

To clearly understand the above binding and fluorescent behaviours between **5** and metal ions, we carried out the ^1H NMR experiments of **5** in the absence or presence of Pb^{2+}. The results obtained are illustrated in Fig. 13 (free **5** in $CDCl_3/CD_3CN$ (1:1.5, v/v) and **5**+1 equiv Pb^{2+} in $CDCl_3/CD_3CN$ (1:1.5, v/v)). For host **5** in $CDCl_3/CD_3CN$, upon the addition of 1 equiv Pb^{2+}, the proton signal of Hd, Hc, was shifted to downfield (see Table 3). Accordingly, the mechanism of complex formation was estimated between **5** and Pb^{2+} in Fig. 14.

3. Conclusions

New fluorogenic calixarene (**5**) bearing two pyrene amine groups has been synthesized and shows selectivity for Cu^{2+} and Pb^{2+}. When Cu^{2+} and Pb^{2+} are bound to **5**, the pyrene monomer and excimer decreased in a ratiometric manner. This ratiometric change is attributable to a combination of heavy metal ion effect, reverse-PET and the conformational changes of the pyrene during the chelation of Cu^{2+} and Pb^{2+} to form a 1:1 complex. Quenching constant and stability constants for complexation of **4** and **5** with Cu^{2+}, Zn^{2+} and Pb^{2+} have been determinated.

4. Experimental

4.1. General

All starting materials and reagents used were of standard analytical grade from Fluka, Merck and Aldrich and used without further purification. Other commercial grade solvents were distilled, and then stored over molecular sieves. The drying agent employed was anhydrous $MgSO_4$. All aqueous solutions were prepared with deionized water that had been passed through a Millipore milli Q Plus water purification system. ^1H and ^{13}C NMR spectra were recorded with a Varian 400 MHz spectrometer in $CDCl_3$ (or $CDCl_3$ and CD_3CN). FT-IR spectra was recorded with a PerkinElmer

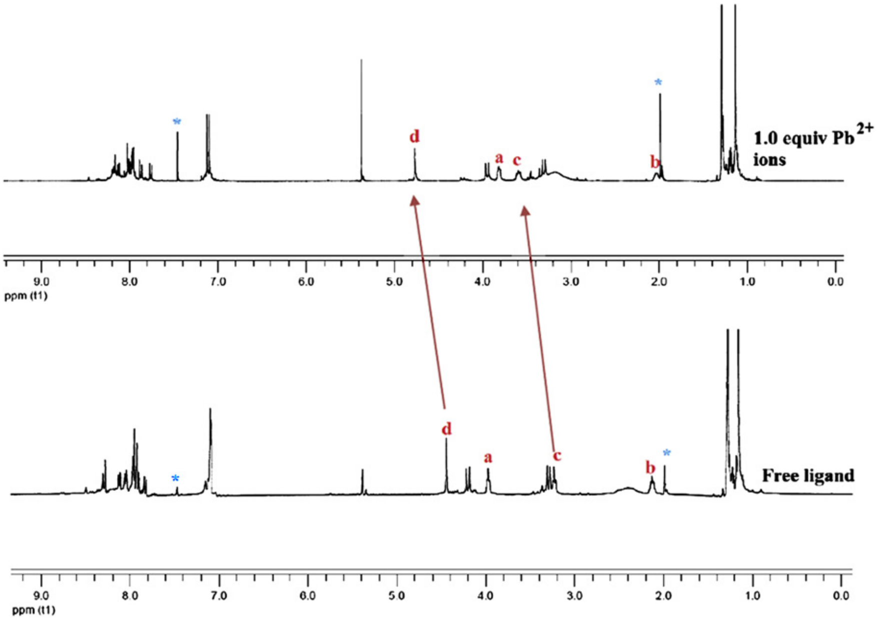


Fig. 13. ^{1}H NMR spectra of receptor **5** (20 mM) upon addition of Pb^{2+} ions (1.0 equiv) in $CDCl_3/CD_3CN$ (1:1.5, v/v) solution, where the asterisk denotes NMR solvent peaks.

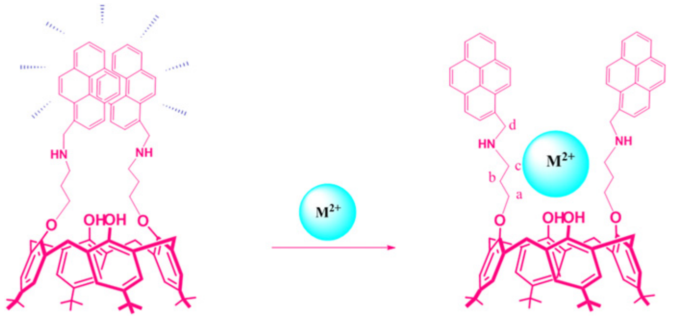


Fig. 14. Possible structures of free **5** and $5{+}M^{2+}$.

Table 3
Chemical shifts of ^{1}H NMR signals of compound **5** (in $CDCl_3/CD_3CN$) in the free form and in the presence of Pb^{2+}

	Chemical shift (ppm) Free **5**	**5**+Pb^{+2}
Hc	3.23	3.60
Hd	4.44	4.76

spectrum 100. UV–vis spectra were obtained on a Perkin–Elmer UV–vis recording spectrophotometer. Fluorescence spectra were recorded on a Perkin–Elmer LS 55 spectrometer. Thin layer chromatography (TLC) was performed using silica gel on glass TLC plates (silica gel H, type 60, Merck).

4.2. Absorption and fluorescence measurements

Absorption spectra of ligands ($1{\times}10^{-6}$ M for fluorescence measurements and $1{\times}10^{-4}$ M for absorption measurements) in CH_3CN/CH_2Cl_2 solutions containing 10 mol equiv of the appropriate metal perchlorate salt were measured using a 1 cm absorption cell. Fluorescence spectra of the same solutions were measured with a 1 cm quartz cell. The excitation wavelength was 350 nm for **4** and 348 nm for **5**. Fluorescence emission spectra were recorded in the range 350–800 nm with a slit width of 5.0 nm. The stoichiometries of the complexes and their stability constants were determined according to a literature procedure.

4.3. Synthesis

Compounds **1**–**3** were synthesized according to the literature.[31–33] The other compounds (**4**–**5**) employed in this work as illustrated in Scheme 1 were synthesized according to the methods given below.

*4.3.1. Synthesis of compound **4**.* To a stirred solution of diamine 3 (0.5 g, 0.65 mmol) in methanol (10 ml) was added a solution of 1-pyrenecarbaldehyde 0.3 g, 1.32 mmol) in THF (10 ml) and refluxed for 6 h to obtain a light yellow precipitate. The precipitate was filtered and washed with methanol. The residue obtained was further recrystallized from dichloromethane/methanol to furnish compound **4**. Yield (0.6 g, 78%), mp 170 °C; IR (KBr, cm^{-1}) 1627 (C=N); ^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 1.01 (s, 18H, $C(CH_3)_3$), 1.33 (s, 18H, $C(CH_3)_3$), 2.62 ((p, J=5.8 Hz, 4H, $CH_2CH_2CH_2$), 3.37 (d, J=13 Hz, 4H, $ArCH_2Ar$), 4.21(t, J=5.8 Hz, 4H, NCH_2), 4.44 (t, J=7.5 Hz, 4H, OCH_2), 4.49 (d, J=13 Hz, 4H, $ArCH_2Ar$), 6.88 (s, 4H, ArH), 7.11 (s, 4H, ArH), 7.46 (d, J=9.9 Hz, 2H, ArH_{Pyr}), 7.81–7.92 (m, 10H, ArH_{Pyr}), 8.04 (d, J=6.6 Hz, 2H, ArH_{Pyr}),8.13 (s, 2H, OH), 8.38 (d, J=8 Hz, 2H, ArH_{Pyr}), 8.52 (d, J=9.5 Hz, 2H, ArH_{Pyr}) 9.54 (s, 2H, CH=N); ^{13}C NMR (400 MHz, $CDCl_3$): 31.30, 31.83, 32.04, 32.24, 34.14, 34.25, 58.59, 73.70, 122.60, 124.50, 124.60, 124.81, 125.48, 125.59, 125.82, 125.92, 127.37, 128.09, 128.32, 128.38, 128.66, 129.88, 130.55, 131.19, 132.70, 133.09, 141.80, 141.19, 150.08, 151.16, 161.25; HRMS found 1186.6587; $C_{84}H_{86}N_2O_4$ requires 1186.6582.

*4.3.2. Reduction of compound **4** (**5**).* To a stirred solution of Schiff base derivative of calixarene **4** (0.5 g, 0.42 mmol) in THF(20 ml) was added $LiAlH_4$ (0.5 g,13.1 mmol) and stirred at room temperature for 6 h. Then the mixture was refluxed for 12 h and added 20 ml water. Dichloromethane (30 ml) was added. The organic layer was separated and washed with water. The organic layer was dried over anhydrous Mg_2SO_4 and filtered. The solvent was evaporated off under reduced pressure. Yield (0.3 g, 60%), mp 132 °C; ^{1}H NMR

($CDCl_3$, 400 MHz) δ (ppm): 0.99 (s, 18H, $C(CH_3)_3$), 1.33 (s, 18H, $C(CH_3)_3$), 2.07 (p, J=6.2 Hz, 4H, $CH_2CH_2CH_2$), 3.18 (t, J=6.6 Hz, 4H, NCH_2), 3.29 (d, J=13 Hz, 4H, $ArCH_2Ar$), 3.96 (t, J=5.6 Hz, 4H, OCH_2), 4.25 (d, J=13 Hz, 4H, $ArCH_2Ar$), 4.43 (s, 4H, CH_2Ar_{Pyr}), 6.84 (s, 4H, ArH), 7.07 (s, 4H, ArH), 7.74 (s, 2H, OH), 7.81 (d, J=9.3Hz, 2H, ArH_{Pyr}), 7.87–7.95 (m, 10H, ArH_{Pyr}), 8.02 (d, J=7.2 Hz, 2H, ArH_{Pyr}), 8.09 (d, J=7.6 Hz, 2H, ArH_{Pyr}), 8.24 (d, J=9.1 Hz, 2H, ArH_{Pyr}); ^{13}C NMR (400 MHz, $CDCl_3$) : 30.59,31.30, 32.04, 32.13, 34.13, 34.26, 47.21, 51.83, 74.77, 123.37, 124.93, 124.98, 125.03, 125.14, 125.41, 125.81, 125.96, 127.16, 127.44, 127.64, 127.77, 127.93, 128.05, 129.23, 130.76, 130.97, 131.44, 133.01, 141.75, 147.16, 149.85, 150.98; HRMS found 1190.6899; $C_{84}H_{90}N_2O_4$ requires 1190.6895.

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References and notes

1. Steed, J. W.; Atwood, J. L. *Supramolecular Chemistry*; John Wiley and Sons: Chichester, 2000.
2. Schneider, H. J.; Yatsimirsky, A. *Principles and Methods in Supramolecular Chemistry*; John Wiley and Sons: Chichester, 2000.
3. Wang, R.; Bu, J.; Liu, J.; Liao, S. *Front. Chem. China* **2008**, *3*, 348–352.
4. Desvergne, J. P.; Czarnik, A. W. *Chemosensors of Ion and Molecule Recognition; NATO ASI Series, Series C*; Kluwer Academic: Dordrecht, The Netherlands, 1997; Vol. 492.
5. Czarnik, A. W. Fluorescent Chemosensors for Ion and Molecule Recognition; ACS Symposium Series 538; American Chemical Society: Washington, DC, 1992.
6. de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J. M.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566.
7. de Silva, A. P.; Gunnlaugsson, T.; McCoy, C. P. *J. Chem. Educ.* **1997**, *74*, 53–58.
8. Bodenant, B.; Weil, T.; Businelli-Pourcel, M.; Fages, F.; Barbe, B.; Pianet, I.; Laguerre, M. *J. Org. Chem.* **1999**, *64*, 7034–7039.
9. Liu, J. M.; Zheng, Q. Y.; Yang, J. L.; Chen, C. F.; Huang, Z. T. *Tetrahedron Lett.* **2002**, *43*, 9209–9212.
10. Hamdi, A.; Kim, S. H.; Abidi, R.; Thué ry, P.; Kim, J. S.; Vicens, J. *Tetrahedron* **2009**, *65*, 2818–2823.
11. Cao, Y. D.; Zheng, Q. Y.; Chen, C. F.; Huang, Z. T. *Tetrahedron Lett.* **2003**, *44*, 4751–4755.
12. Kim, H. J.; Kim, J. S. *Tetrahedron Lett.* **2006**, *47*, 7051–7055.
13. Memon, S.; Akceylan, E.; Sap, B.; Tabakci, M.; Roundhill, D. M.; Yilmaz, M. *J Polym. Environ.* **2003**, *11*, 67–69.
14. Sirit, A.; Karakucuk, A.; Memon, S.; Kocabas, E.; Yilmaz, M. *Tetrahedron: Asymmetry* **2004**, *15*, 3595–3600.
15. (a) Bozkurt, S.; Karakucuk, A.; Sirit, A.; Yilmaz, M. *Tetrahedron* **2005**, *61*, 10443–10448; (b) Kocabas, E.; Karakucuk, A.; Sirit, A.; Yilmaz, M. *Tetrahedron: Asymmetry* **2006**, *17*, 1514–1520; (c) Yilmaz, A.; Tabakci, B.; Akceylan, E.; Yilmaz, M. *Tetrahedron* **2007**, *63*, 5000–5005.
16. Ediz, O.; Tabakci, M.; Memon, S.; Yilmaz, M.; Roundhill, D. M. *Supramol. Chem.* **2004**, *16*, 199–204.
17. Durmaz, M.; Alpaydin, S.; Sirit, A.; Yilmaz, M. *Tetrahedron: Asymmetry* **2006**, *17*, 2322–2327.
18. Ocak, U.; Ocak, M.; Surowiec, K.; Bartsch, R. A.; Gorbunova, M. G.; Tu, C.; Surowiec, M. A. *J. Inclusion Phenom. Macrocyclic Chem.* **2009**, *63*, 131–139.
19. Broan, C. J. *Chem. Commun.* **1996**, 699–700.
20. (a) Aoki, I.; Sakaki, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1992**, 730–732; (b) Bu, J.-H.; Zheng, Q.-Y.; Chen, C.-F.; Huang, Z.-T. *Org. Lett.* **2004**, *6*, 3301–3303.
21. (a) Leray, I.; Lefevre, J.-P.; Delouis, J.-F.; Delaire, J.; Valeur, B. *Chem.—Eur. J.* **2001**, *7*, 4590–4598; (b) Kim, S. K.; Bok, J. H.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Org. Lett.* **2005**, *7*, 4839–4842; (c) Choi, J. K.; Kim, S. H.; Yoon, J.; Lee, K.-H.; Bartsch, R. A.; Kim, J. S. *J. Org. Chem.* **2006**, *71*, 8011–8015.
22. (a) Jin, T.; Ichikawa, K.; Koyana, T. *J. Chem. Soc., Chem. Commun.* **1992**, 499–501; (b) Kim, S. K.; Lee, S. H.; Lee, J. Y.; Lee, J. Y.; Bartsch, R. A.; Kim, J. S. *J. Am. Chem. Soc.* **2004**, *126*, 16499–16506; (c) Schazmann, B.; Alhashimy, N.; Diamond, D. *J. Am. Chem. Soc.* **2006**, *128*, 8607–8614.
23. (a) Jin, T. *Chem. Commun.* **1999**, 2491–2492; (b) Castellano, R. K.; Craig, S. L.; Nuckolls, C.; Rebek, J., Jr. *J. Am. Chem. Soc.* **2000**, *122*, 7876–7882.
24. Chang, K. C.; Su, I. H.; Senthilvelan, A.; Chung, W. S. *Org. Lett.* **2007**, *9*, 17.
25. Kim, H. J.; Park, S. Y.; Yoon, S.; Kim, J. S. *Tetrahedron* **2008**, *64*, 1294–1300.
26. Kumar, M.; Babu, J. N.; Bhalla, V.; Kumar, R. *Sens. Actuators, B* **2010**, *144*, 183–191.
27. (a) Boening, D. W. *Chemosphere* **2000**, *40*, 1335–1351; (b) Mohan, D.; Gupta, V. K.; Srivasta, S. K.; Chander, S. *Colloids Surf., A* **2001**, *177*, 169–181; (c) Yardim, M. F.; Budinova, T.; Ekinci, E.; Petrov, N.; Razvigorova, M.; Minkova, V. *Chemosphere* **2003**, *52*, 835–841; (d) Harris, H. H.; Pickering, I. J. P.; George, G. N. *Science* **2003**, *301,* 1203–1203.
28. (a) Linder, M. C.; Hazegh-Azam, M. *Am. J. Clin. Nutr.* **1996**, *63*, 797S–811S; (b) Uauy, R.; Olivares, M.; Gonzalez, M. *Am. J. Clin. Nutr.* **1998**, *67*, 952S–959S.
29. (a) Harris, Z. L.; Gitlin, J. D. *Am. J. Clin. Nutr.* **1996**, *63*, 836S–845S; (b) Scheinberg, I. H.; Sternlieb, I. *Am. J. Clin. Nutr.* **1996**, *63*, 842S–845S.
30. Kumar, R.; Bhalla, V.; Kumar, M. *Tetrahedron* **2008**, *64*, 8095–8101.
31. Gutsche, C. D.; Iqbal, M.; Steward, D. *J. Org. Chem* **1986**, *51*, 742–745.
32. Métay, E.; Duclos, M. C.; Pellet-Rostaing, S.; Lemaire, M.; Schulz, J.; Kannappan, R.; Bucher, C.; Saint-Aman, E.; Chaix, C. *Eur. J. Org. Chem.* **2008**, 4304–4312.
33. Chrisstoffels, L. A. J.; de Jong, F.; Reinhoudt, D. N.; Sivelli, S.; Gazzola, L.; Casnati, A.; Ungaro, R. *J. Am. Chem. Soc.* **1999**, *121*, 10142–10151.
34. Murphy, C. B.; Zhang, Y.; Troxler, T.; Ferry, V.; Martin, J. J.; Jones, W. E. *J. Phys. Chem. B* **2004**, *108*, 1537–1543.
35. Larsen, R. W.; Helms, M. K.; Everett, W. R.; Jameson, D. M. *Photochem. Photobiol.* **1999**, *69*, 429–434.
36. Ocak, U.; Ocak, M.; Surowiec, K.; Liu, X.; Bartsch, R. A. *Tetrahedron* **2009**, *65*, 7038–7047.
37. Bourson, J.; Valeur, B. *J. Phys. Chem.* **1989**, *93*, 3871–3876.
38. Valeur, B. *Molecular Fluorescence Principles and Applications*; Wiley-VCH: 2001.