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F^--Induced 'turn-on' fluorescent chemosensor based on 1,3-*alt* thiacalix[4]arene

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ABSTRACT

A new thiacalix[4]arene based fluorescent sensor **1** bearing two naphthyl groups has been synthesized in 1,3-*alternate* conformation. In the absence of fluoride ion, the receptor **1** is in 'off-state' showing no fluorescence emission. The presence of fluoride ion triggered the fluorescence emission to 'on-state'. The receptor shows pronounced selectivity for fluoride ions. In THF, the presence of F^- ions induces the formation of a 1:1 (G:H) complex.

1. Introduction

The selective recognition and sensing of anions by artificial optical receptors have emerged as a key research theme within the host–guest chemistry.[1] Among the biologically important anions, fluoride is of particular interest owing to its role in preventing dental caries[2] and in the treatment for osteoporosis.[3] Furthermore, F^- ions are also associated with anaesthetics, hypnotics, psychiatric drugs, nerve gases, in the analysis of drinking water, and in the refinement of uranium used in nuclear weapon manufacture.[4] An excess of fluoride can lead to thyroid activity depression and immune system disruption and fluorosis,[5] which is a type of fluoride toxicity that generally manifests itself clinically in terms of an increase in bone density. Thus, due to diversity of its functions, both beneficial and otherwise, the detection of fluoride ions becomes important. The detection and monitoring of anions by methods, which allow the development of selective and sensitive assays are in great demand. Fluorescence signalling is one of the first choices due to its high detection sensitivity and simplicity[6] over the other spectroscopic methods. Thus, designing fluorescent sensors for fluoride[7] has recently drawn worldwide attention. The basic design of these fluorescent sensors consists of an ionophore for selective ion binding and a fluorophore,[8] which convert binding signal of ionophore unit into a highly sensitive light signal through changes in fluorescence emission. Thus, while designing sensors the recognition unit linked to fluorophore should be carefully examined because the recognition unit is responsible for the selectivity and binding efficiency of the chemosensor. The recognition unit of the receptors containing the polarized NH fragment behaves as H-bond donors towards anion and is widely used as receptors for recognition and sensing purpose.[9] The urea and thiourea moieties provide such effective and directional H-bonds for anion recognition. The urea and thiourea subunits can establish two directional H-bonds with the Y-shaped carboxylate groups or chelate spherical anions (e.g., halides). The H-bond donating tendencies of a given donor group are in some way related to its protonic acidity. Thiourea is a stronger acid than urea (pK_a=21.1 and 26.9, respectively),[10] thus it is expected that thiourea containing receptors establish stronger H-bond interactions and form more stable complexes with anions than their urea containing counterparts.

Most of the fluoride selective receptors containing different fluorogenic units mainly involve fluorescence quenching mechanism such as photo-induced electron transfer (PET)[11] on interaction with fluoride ions. The fluorescence quenching mechanisms are susceptible to static and collisional quenching by non-analyte species, which are prevalent and unavoidable in biological systems;[12] consequently, the accuracy of fluorescent probes involving quenching mechanism for anions is poor. On the other hand, the fluorescence enhancement rather than quenching is usually preferred in order to observe a high signal output. Only a few sensors in which the binding of F^- ion causes an increase in the fluorescence emission have been reported.[13] James et al.[14] reported boronic acid based ditopic receptors for potassium fluoride. The presence of potassium fluoride 'switches on' the fluorescence of ditopic receptors and fluorescence can be 'switched off' by removing the potassium cation from crown ether unit of the receptors. However, the system is non-fluorescent in the presence of only fluoride ion. Kim et al.[15] have reported (hydroxyphenyl)benzoxazole receptor

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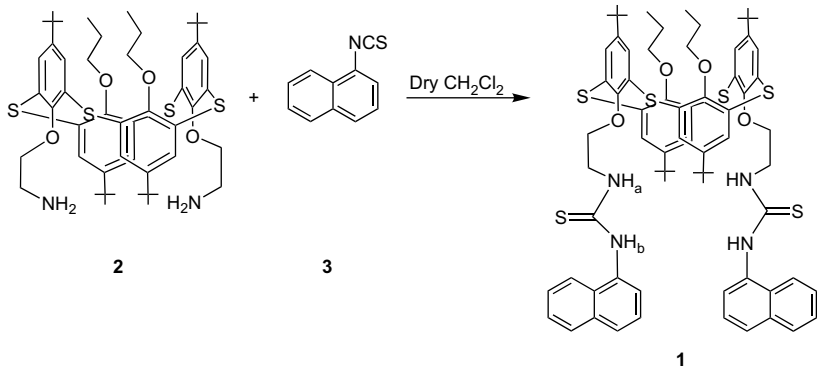

Scheme 1.

containing urea groups as gelator, which changed to a solution with strong greenish fluorescence in the presence of fluoride ion. Yoon et al.[16] have reported fluorescent sensors for fluoride ion describing an internal charge transfer mechanism having anthracene and naphthalimide fluorophore.

Calix[4]arene[17] scaffold with appropriate binding sites has been utilized for various ion-sensing properties.[18] The fluorescent chemosensors based on calix[4]arene bearing different binding sites such as amide,[19] urea,[20] and thiourea[21] have been reported utilizing different photophysical processes such as photo-induced electron transfer (PET),[19a–c] photo-induced charge transfer (PCT),[19d,e] excimer/exciplex formation, and extinction.[19a,e] Diamond et al.[20] have reported a fluorescent optical chemosensor for chloride based on 1,3-*alternate* conformation of tetra-substituted calix[4]arene bearing urea moieties. The presence of chloride ion triggers the conformational changes, which resulted in ratiometric sensing of chloride ion.

Recently, thiacalix[4]arene[22] reported as the second member of the calixarene[17] family has been extensively used for the recognition of cations[23] and their potential applications as fluorescence sensing agents have received much interest. Compared to cation recognition, the anion recognition of thiacalix[4]arene series[24] is much less explored. Lhotak et al.[24] have reported thiacalix[4]arene based anion receptors bearing urea/thiourea on lower/upper rim. These anionic receptors showed poor discrimination between various anions.

Our research involves design, synthesis and evaluation of calix[4]arene and thiacalix[4]arene based receptors selective for soft metal ions[25] and anions.[26] Recently, we reported[26a,b] chloride selective sensors based on calix[4]arene possessing urea moieties. Now we have designed and synthesized fluoride ion selective fluorescent chemosensor **1** based on 1,3-*alternate* conformation of thiacalix[4]arene framework possessing thiourea moieties conjugated with naphthyl fluorophore. The fluorescence emission of compound **1** was in 'off-state', i.e., completely quenched. The addition of fluoride ion to the solution of compound **1** results in the fluorescence emission, i.e. 'on-state.' The fluoroionophore **1** shows high selectivity for fluoride ion with a detection limit[27] of 2.6×10^{-7} mol L^{-1}. To the best of our knowledge this is the first report where thiacalix[4]arene scaffold has been combined with naphthyl moieties to prepare fluorescent sensor for fluoride ions. While we were writing this paper, Kim et al.[28] have reported a fluorescent chemosensors for fluoride based on anthraquinone appended calix[4]arene bearing amide groups.

2. Results and discussion

The condensation of thiacalix[4]arene-1,3-diamine **2**[25d] in the 1,3-*alternate* conformation with 2.0 mol equiv of 1-naphthylisothiocyanate **3** in dichloromethane furnished thiacalix[4]arene podand **1** in 42% yield (Scheme 1).

The structure of **1** was confirmed from its spectroscopic and analytical data. The IR spectrum of compound **1** showed a C=S stretching band at 1520 cm^{-1}. The FAB mass spectrum showed a parent ion peak at 1262 (M^+) corresponding to a 1:2 condensation product. The ^1H NMR spectrum of compound **1** showed two singlets (18H each) corresponding to *tert*-butyl protons, one broad (4H) for NCH_2 protons, one triplet (4H) for OCH_2, one broad (4H) for

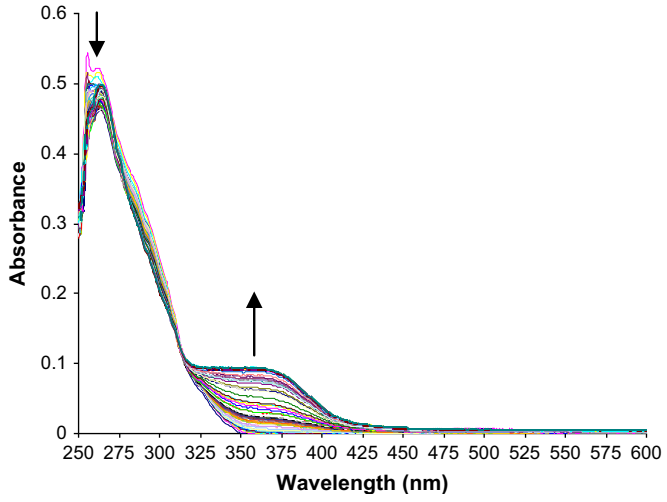

Figure 1. Absorption spectra of compound **1** (6.0 μM) on addition of F^- (0–100 equiv, 0–600 μM) in DMSO.

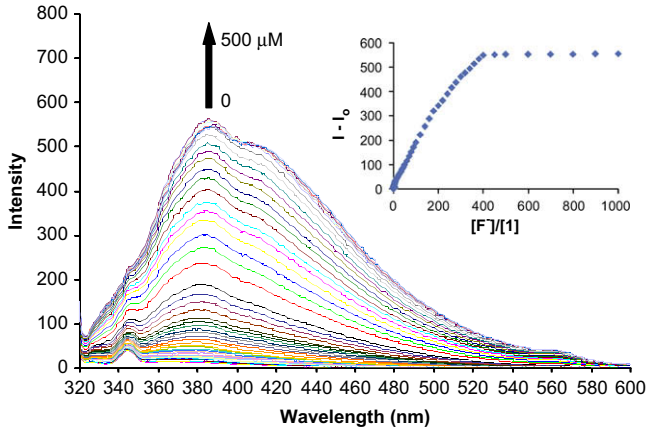

Figure 2. Fluorescent emission spectra of compound **1** (1.0 μM) in the presence of different concentration of F^- (0–500 μM) in THF. Excitation wavelength was 310 nm. Inset: binding isotherm at 385 nm.

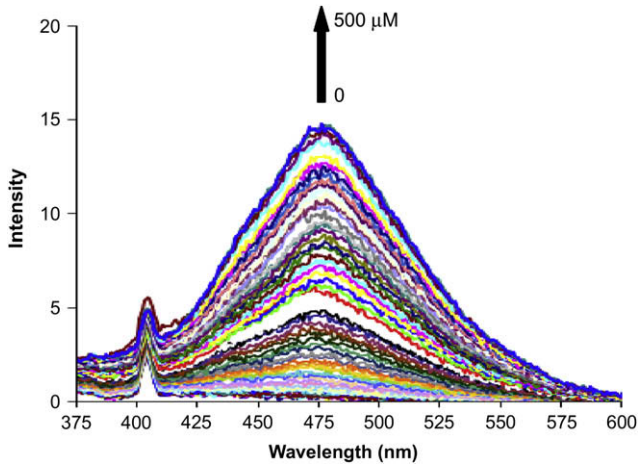

Figure 3. Fluorescent emission spectra of compound **1** (1.0 μM) in the presence of different concentration of F^- (0–500 μM) in THF. Excitation wavelength was 360 nm.

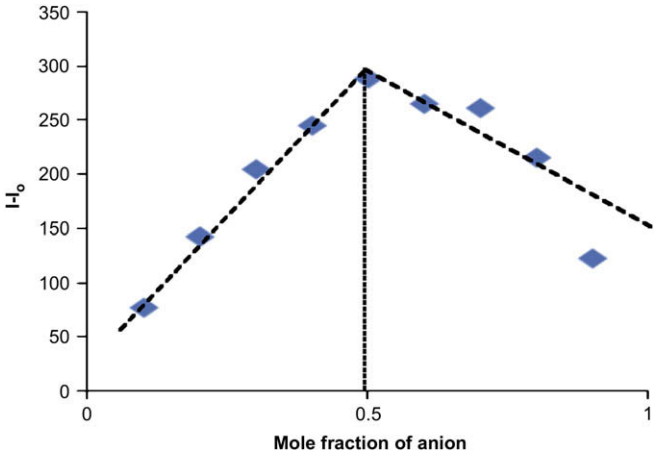

Figure 5. Job plot for **1** and F^- $[1+F^-]=2.50\times10^{-5}$ M in THF.

OCH_2 protons, two singlets (4H each) for aromatic protons and one broad singlet and one singlet (2H each) for thiourea protons.

The anion binding properties of compound **1** were investigated by UV–vis, fluorescence and ^1H NMR spectroscopy. The UV–vis titrations were carried out in DMSO and fluorescence titrations were carried out in tetrahydrofuran by adding aliquots of solutions of different anions. The UV–vis spectrum of compound **1** exhibits typical absorption band of naphthalene at λ 257 nm in DMSO. The addition of increasing amounts of fluoride ion (1.0–100 equiv) to the solution of compound **1** in DMSO resulted in decrease in absorption at 257 nm and formation of new red shifted absorption band at λ 360 nm (Fig. 1).

Compound **1** did not show any fluorescence emission band when excited at 310 nm. The quenched fluorescence emission of compound **1** indicates its 'off-state'. Upon addition of increasing amounts of F^- ion (1.0–500 equiv) to the solution of compound **1**, a significant increase in fluorescence emission at λ 385 nm with a shoulder at λ 412 nm was observed (Fig. 2). The increase in fluorescence emission (Fig. 2) of compound **1** with F^- ion was attributed to $1/F^-$ complex. The increase in fluorescence emission induced by F^- ion is ascribed to intramolecular excimer formation[29] between two naphthyl moieties. The intermolecular binding interactions of F^- ion with NH protons of thiourea moieties trigger the intramolecular π–π interactions of naphthyl groups, which lead to excimer formation. The 'off-state' of free ligand **1** turns to 'on-state' with the addition of F^- ion. Likewise, compound **1** did not show any fluorescence emission band when excited at 360 nm, however on addition of fluoride ions (1.0–500 equiv), a new red shifted emission band appears at 476 nm (Fig. 3). This red shifted fluorescence emission band is related to the red shift of absorption peak upon the addition of fluoride ion.[13c] Under the same conditions as used above for F^- ion, we also tested the fluorescence response to other anions like Cl^-, Br^-, I^-, OAc^-, HSO_4^-, NO_3^-, $H_2PO_4^-$, malonate, fumarate, succinate, tartrate, adipate, phthalate beside F^- ion; as shown in Figure 4, no significant fluorescence change of **1** occurred in the presence of (500 μM) of other anions except in the case of OAc^- and HSO_4^- ions where a small enhancement in the fluorescence was observed.

In order to determine the stoichiometry of the **1**–F^- complex, the method of continuous variation (Job plot) was also used. The total concentration of compound **1** and F^- was constant (2.5×10^{-5} M), with a continuous variable molar fraction of guest ($[F^-]/[\mathbf{1}]+[F^-]$). Figure 5 shows the job plot of compound **1** with F^- ion. The **1**–F^- complex concentration approaches a maximum when the molar fraction of F^- is 0.5, which means **1** and F^- formed a 1:1 complex (Fig. 5). The association constant (log β) of compound **1** for F^- ions was calculated from fluorescence titration experiments by means of SPECFIT programme (global analysis system V3.0 for 32-bit Window system), which uses singular value decomposition and non-linear regression modelling by the Leverberg–Marquardt method[30] and was found to be 3.02 ± 0.09 M^{-1}.

To test the practical applicability of compound **1** as F^- selective fluorescent sensor, competitive experiments were carried out in

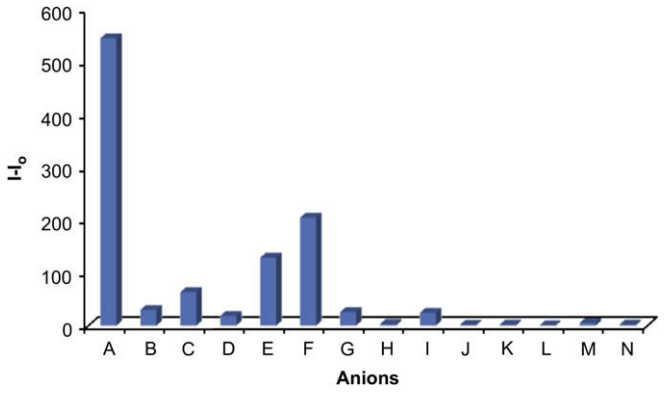

Figure 4. Fluorescence enhancement ($I-I_o$) of compound **1** (1.0 μM) at 385 nm upon addition of different anions (500 equiv, 500 μM) in THF. A=F^-, B=Cl^-, C=Br^-, D=I^-, E=OAc^-, F=HSO_4^-, G=NO_3^-, H=$H_2PO_4^-$, I=malonate, J=fumarate, K=succinate, L=tartrate, M=adipate, N=phthalate.

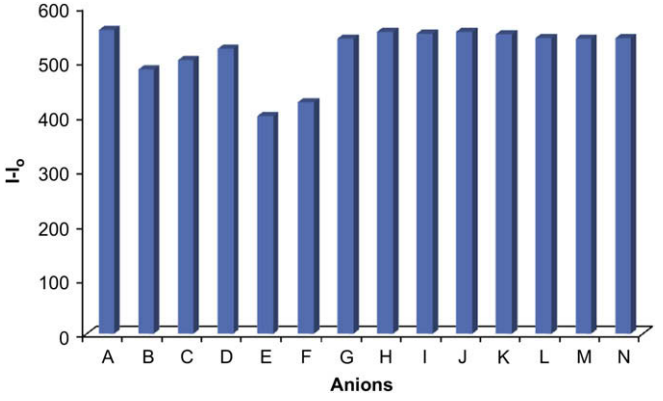

Figure 6. Competitive selectivity of compound **1** (1.0 μM) towards F^- (A, 500 equiv, 500 μM) in the presence of other anions (B–N, 500 equiv, 500 μM) in THF. A=F^-, B=Cl^-, C=Br^-, D=I^-, E=OAc^-, F=HSO_4^-, G=NO_3^-, H=$H_2PO_4^-$, I=malonate, J=fumarate, K=succinate, L=tartrate, M=adipate, N=phthalate.

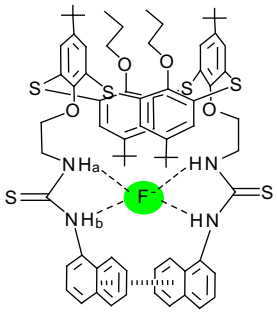

Figure 7. Proposed π-interactions between two naphthyl moieties upon addition of F^- ion.

the presence of F^- at 500 μM mixed with Cl^-, Br^-, I^-, OAc^-, HSO_4^-, NO_3^-, $H_2PO_4^-$, malonate, fumarate, succinate, tartrate, adipate, phthalate at 500 μM; as shown in Figure 6, no significant variation in fluorescence intensity change ($I-I_o$) was found by comparison with or without the other anions besides F^- ion except for OAc^- and HSO_4^-, which interfere with the detection of F^- ions. This means that compound **1** has high selectivity for F^- ion over other studied anions.

Further, the intermolecular binding interactions of compound **1** with F^- ion were studied using ^1H NMR spectroscopy in DMSO-d_6. The ^1H NMR spectrum of compound **1** shows two singlets at 9.30 ppm and 9.67 ppm due to NH_a and NH_b protons, respectively. It was found that on addition of small amount (0.5 equiv) of tetrabutylammoniun fluoride to the solution of compound **1**, there were remarkable downfield shifts in NH_a protons from 9.30 ppm to 9.72 ppm and NH_b protons from 9.67 ppm to 9.80 ppm. The downfield shifts demonstrate the hydrogen bonds formed between thiourea NH protons and fluoride ion. There was no change in chemical shift of naphthyl protons with the addition of fluoride ion. The interaction of fluoride ion with compound **1** leads to excimer formation between two naphthyl moieties (Fig. 7).

3. Conclusion

In conclusion, we developed a selective fluorescent chemosensor **1** for fluoride ion based on thiacalix[4]arene armed with two naphthyl moieties. In the absence of fluoride ion, the receptor **1** was in 'off-state' showing no fluorescence emission band. With the addition of fluoride ion, the fluorescence emission turned to 'on-state'. The receptor **1** showed pronounced selectivity for fluoride ions and may be considered as potential fluorescent chemosensor for fluoride ion. Work is in progress to explore sensors for other anions based on thiacalix[4]arenes/calix[4]arenes armed with different fluorophores.

4. Experimental section

4.1. General

The ^1H and ^{13}C NMR spectra were recorded on JEOL 300 MHz spectrometer using TMS as internal standard and $CDCl_3$ as solvent. FAB mass spectra were recorded on JEOL XS102/DA-6000 mass spectrometer using xenon (6 kV, 10 mA) as FAB gas. Infrared spectra were recorded on a Pye Unicam SP3-3 Infrared spectrophotometer. UV–vis and fluorescence spectra were recorded with Shimadzu UV-2450 PC spectrophotometer and Shimadzu RF-5301(PC) spectrofluorophotometer, respectively. Elemental analysis was done at Department of Chemistry, Guru Nanak Dev University, Amritsar using ThermoFinnigan Elemental Analyzer (Model Flash EA 1112). Stock solutions (0.1 M) of anions as their tetrabutylammonium salts were prepared in THF. Stock solution (0.01 mM) of compound **1** was prepared in THF. For all measurements of fluorescence spectra, excitation wavelengths were 310 nm and 360 nm and slit width was 3.0 nm. UV–vis and fluorescence spectra were performed by using 6.0 μM and 1.0 μM of compound **1** in DMSO and THF and varying concentration of guests (anion).

4.2. Synthesis of 1

To a solution of thiacalix[4]arene-1,3-diamine **2** (200 mg, 0.225 mmol) in 30 ml of dry CH_2Cl_2 was added 1-naphthylisothiocyanate **3** (83 mg, 0.450 mmol). The reaction mixture was stirred at room temperature for 48 h. After completion of reaction (TLC) the solvent was removed in vacuum. The residue was recrystallised from dichloromethane and methanol (1:4) to give 0.118 g (42%) of **1** as off white solid; mp 214–216 °C. [Found: C, 68.43; H, 6.39. $C_{72}H_{84}N_4O_4S_6$ requires: C, 68.57; H, 6.67.] R_f (3:7, ethyl acetate/hexane) 0.55; ν_{max} (solid, KBr pallet) 1520 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.94–7.87 (8H, m, ArH×8), 7.80 (2H, s, NH×2), 7.52–7.42 (6H, m, ArH×6), 7.31 (2H, d, J=7.2 Hz, ArH×2), 7.13 (4H, s, ArH×4), 6.93 (4H, s, ArH×4), 6.76 (2H, br, NH×2), 3.87 (4H, br, OCH_2×2), 3.59 (4H, t, J=7.5 Hz, OCH_2×2), 3.37 (4H, br, NCH_2×2), 1.22 (18H, s, $C(CH_3)_3$×2), 1.07 (18H, s, $C(CH_3)_3$×2), 1.01–0.86 (4H, m, CH_2×2), 0.59 (6H, t, J=7.5 Hz, CH_3×2). ^{13}C NMR (300 MHz, $CDCl_3$): δ 181.8, 156.8, 156.7, 146.0, 144.7, 134.8, 131.9, 130.1, 129.1, 128.5, 127.9, 127.8, 127.3, 126.8, 126.5, 125.7, 125.2, 122.4, 70.2, 69.9, 45.4, 34.0, 31.1, 21.8, 9.8; FABMS: m/z 1262 (M^+).

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References and notes

1. (a) Sessler, J. L.; Davis, J. M. *Acc. Chem. Res.* **2001**, *34*, 989–997; (b) Gale, P. A. *Coord. Chem. Rev.* **2000**, *199*, 181–233; (c) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486–516; (d) Gale, P. A. *Coord. Chem. Rev.* **2001**, *213*, 79–128; (e) Suksai, C.; Tuntulani, T. *Chem. Soc. Rev.* **2003**, *32*, 192–202; (f) Martinez-Manez1, R.; Sancenón, F. *J. Fluoresc.* **2005**, *15*, 267–285; (g) Gunnlaugsson, T.; Glynn, M.; Tocci, G. M.; Kruger, P. E.; Pfeffer, F. M. *Coord. Chem. Rev.* **2006**, *250*, 3094–3117.
2. Kirk, K. L. *Biochemistry of Halogens and Inorganic Halides*; Plenum: New York, NY, 1991; p 58.
3. Kleerekoper, M. *Endocrinol. Metab. Clin. North Am.* **1998**, *27*, 441–452.
4. (a) Waldbott, G. *Clin. Toxicol.* **1981**, *18*, 531–541; (b) Matuso, S.; Kiyomiya, K.-i.; Kurebe, M. *Arch. Toxicol.* **1998**, *72*, 798–806; (c) Zhang, S.-W.; Swager, T. M. *J. Am. Chem. Soc.* **2003**, *125*, 3420–3421; (d) Riggs, B. L. *J. Bone Miner. Res.* **1984**, 366–393; (e) Laisalmi, M.; Kokki, H.; Soikkeli, A.; Markkanen, H.; Yli-Hankala, A.; Rosenberg, P.; Lindgren, L. *Acta Anaesthesiol. Scand.* **2006**, *50*, 982–987.
5. (a) Wiseman, A. *Handbook of Experimental Pharmacology XX/2*; Springer: Berlin, 1970; Part 2, pp 48–97; (b) Weatherall, J. A. Pharmacology of Fluorides. In *Handbook Experimental Pharmacology XX/1*; Springer: Berlin, 1969; Part 1, pp 141–172; (c) Dreisbuch, R. H. *Handbook of Poisoning*; Lange Medical: Los Altos, CA, 1980.
6. (a) de Silva, A. P.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Huxley, A. J.; McCoy, C. P.; Rademacher, J. T.; Rice, T. E. *Chem. Rev.* **1997**, *97*, 1515–1566; (b) Fabbrizzi, L.; Poggi, A. *Chem. Soc. Rev.* **1995**, *24*, 197–202; (c) Valeur, B.; Leray, I. *Inorg. Chim. Acta* **2007**, *360*, 765–774; (d) Kim, S. H.; Kim, H. J.; Yoon, J.; Kim, J. S. In *Calixarenes in the Nanoworld*; Vicens, J., Harrowfield, J., Eds.; Springer: Dordrecht, The Netherlands, 2007; Chapter 15; (e) Valeur, B.; Bourson, J.; Pouget, J.; Czarnik, A. W. Fluorescent Chemosensors for Ion and Molecule Recognition. In *ACS Symposium Series 538*; American Chemical Society: Washington, DC, 1993; (f) Sharp, S. L.; Warmack, R. J.; Goudonnet, J. P.; Lee, I.; Ferrell, T. L. *Acc. Chem. Res.* **1993**, *26*, 377–382.
7. (a) Dusemund, C.; Sandanayake, K. R. A. S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1995**, 333–334; (b) Yamamoto, H.; Ori, A.; Ueda, K.; Dusemund, C.; Shinkai, S. *Chem. Commun.* **1996**, 407–408; (c) Scherer, M.; Sessler, J. L.; Gebauer, A.; Lynch, V. *Chem. Commun.* **1998**, 85–86; (d) Anzenbacher, P., Jr.; Jursikova, K.; Lynch, V. M.; Gale, P. A.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 11020–11021; (e) Nicolas, M.; Fabre, B.; Simonet, J. *Chem. Commun.* **1999**, 1881–1882; (f) Camiolo,

S.; Gale, P. A. *Chem. Commun.* **2000**, 1129–1130; (g) Lee, D. H.; Im, J. H.; Lee, J. H.; Hong, H. I. *Tetrahedron Lett.* **2002**, *43*, 9637–9640; (h) Yun, S.; Ihm, H.; Kim, H. G.; Lee, C. W.; Indrajit, B.; Oh, K. S.; Gong, Y. J.; Lee, J. W.; Yoon, J.; Lee, H. C.; Kim, K. S. *J. Org. Chem.* **2003**, *68*, 2467–2470.

8. (a) Valeur, B.; Leray, I. *Coord. Chem. Rev.* **2000**, *205*, 3–40; (b) Nohta, H.; Satozono, H.; Koiso, K.; Yoshida, H.; Ishida, J.; Yamaguchi, M. *Anal. Chem.* **2000**, *72*, 4199–4202; (c) Okamoto, A.; Ichiba, T.; Saito, I. *J. Am. Chem. Soc.* **2004**, *126*, 8364–8365.
9. (a) Bianchi, A.; Bowman-James, K. In *Supramolecular Chemistry of Anions*; Garcia-Espana, E., Ed.; Wiley-VCH: New York, NY, 1997; (b) Hay, B. P.; Firman, T. K.; Moyer, B. A. *J. Am. Chem. Soc.* **2005**, *127*, 1810–1819.
10. Bordwell, F. G. *Acc. Chem. Res.* **1988**, *21*, 456–463.
11. (a) Fabbrizzi, L.; Faravelli, H.; Franzese, G.; Licchelli, M.; Perotti, A.; Taglietti, A. *Chem. Commun.* **1998**, 971–972; (b) Cooper, C. R.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, 1365–1366; (c) Arimori, S.; Davidson, M. G.; Fyles, T. M.; Hibbert, T. G.; James, T. D.; Kociok-Köhn, G. I. *Chem. Commun.* **2004**, 1640–1641; (d) Galbraith, E.; Fyles, T.; Marken, M. F.; Davidson, M. G.; James, T. D. *Inorg. Chem.* **2008**, *47*, 6236–6244; (e) Kim, S. K.; Yoon, J. *Chem. Commun.* **2002**, 770–771.
12. Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer Academic/Plenum: New York, NY, 1999; pp 238–264.
13. (a) Tong, H.; Wang, L.; Jing, X.; Wang, F. *Macromolecules* **2003**, *36*, 2584–2586; (b) Lu, H.; Xu, W.; Zhang, D.; Chen, C.; Zhu, D. *Org. Lett.* **2005**, *7*, 4629–4632; (c) Lee, J. Y.; Cho, E. J.; Mukamel, S.; Nam, K. C. *J. Org. Chem.* **2004**, *69*, 943–950; (d) Xu, G.; Tarr, M. A. *Chem. Commun.* **2004**, 1050–1051; (e) Oton, F.; Tárraga, A.; Velasco, M. D.; Espinosa, A.; Molina, P. *Chem. Commun.* **2004**, 1658–1659; (f) Liu, C.; Qian, X.; Sun, G.; Zhao, L.; Li, Z. *New J. Chem.* **2008**, *32*, 472–476; (g) Hudnall, T. W.; Gabbai, F. P. *Chem. Commun.* **2008**, 4596–4597; (h) Panzella, L.; Pezzella, A.; Arzillo, M.; Manini, P.; Napolitano, A.; d'Ischia, M. *Tetrahedron* **2009**, *65*, 2032–2036; (i) Swamy, K. M. K.; Lee, Y. J.; Lee, H. N.; Chun, J.; Kim, Y.; Kim, S.-J.; Yoon, J. *J. Org. Chem.* **2006**, *71*, 8626–8628.
14. Koskela, S. J. M.; Fyles, T. M.; James, T. D. *Chem. Commun.* **2005**, 945–947.
15. Kim, T. H.; Choi, M. S.; Sohn, B.-H.; Park, S.-Y.; Lyoo, W. S.; Lee, T. S. *Chem. Commun.* **2008**, 2364–2366.
16. (a) Jun, E. J.; Swamy, K. M. K.; Bang, H.; Kim, S.-J.; Yoon, J. *Tetrahedron Lett.* **2006**, *47*, 3103–3106; (b) Xu, Z.; Kim, S.; Kim, H. N.; Han, S. J.; Lee, C.; Kim, J. S.; Qian, X.; Yoon, J. *Tetrahedron Lett.* **2007**, *48*, 9151–9154.
17. (a) Gutsche, C. D. Calixarenes. In *Monographs in Supramolecular Chemistry*; Stoddart, J. F., Ed.; Royal Society of Chemistry: Cambridge, UK, 1989; Vol. 1; (b) *Calixarenes: A Versatile Class of Macrocyclic Compounds*; Vicens, J., Bohmer, V., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; (c) Gutsche, C. D. *Calixarenes Revisited. Monographs in Supramolecular Chemistry*; The Royal Society of Chemistry: Cambridge, UK, 1998; Vol. 6; (d) *Calixarenes 50th Anniversary: Commemorative Issue*; Vicens, J., Asfari, Z., Harrowfield, J. M., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 1994; (e) Calixarene Molecules for Separations. In *ACS Symposium Series*; Lumetta, G. J., Rogers, R. D., Eds.; American Chemical Society: Washington, DC, 1999.
18. (a) Kim, J. S.; Quang, D. T. *Chem. Rev.* **2007**, *107*, 3780–3799; (b) Lee, M. H.; Quang, D. T.; Jung, H. S.; Yoon, J.; Lee, C.-H.; Kim, J. S. *J. Org. Chem.* **2007**, *72*, 4242–4245; (c) Miyaji, H.; Sato, W.; Sessler, J. L. *Angew. Chem., Int. Ed.* **2000**, *39*, 1777–1780; (d) Piateka, P.; Jurczak, J. *Chem. Commun.* **2002**, 2450–2451; (e) Ludwig, R. *Fresenius' J. Anal. Chem.* **2000**, *367*, 103–128; (f) Chellappan, K.; Singh, N. J.; Hwang, I. C.; Lee, J. W.; Kim, K.-S. *Angew. Chem., Int. Ed* **2005**, *44*, 2899–2903.
19. (a) Kim, H. J.; Kim, S. K.; Lee, J. Y.; Kim, J. S. *J. Org. Chem.* **2006**, *71*, 6611–6614; (b) Miao, R.; Zheng, Q.-Y.; Chen, C-F.; Huang, Z.-T. *Tetrahedron Lett.* **2005**, *46*, 2155–2158; (c) Lee, S. H.; Kim, S. H.; Kim, S. K.; Jung, J. H.; Kim, J. S. *J. Org. Chem.* **2005**, *70*, 9288–9295; (d) Lee, S. H.; Kim, H. J.; Lee, Y. O.; Vicens, J.; Kim, J. S. *Tetrahedron Lett.* **2006**, *47*, 4373–4376; (e) Kim, S. K.; Bok, J. H.; Bartsch, R. A.; Lee, J. Y.; Kim, J. S. *Org. Lett.* **2005**, *7*, 4839–4842.
20. Schazmann, B.; Alhashimy, N.; Diamond, D. *J. Am. Chem. Soc.* **2006**, *128*, 8607–8614.
21. Liu, S.-Y.; He, Y.-B.; Wu, J.-L.; Wei, L.-H.; Qin, H.-J.; Meng, L.-Z.; Hu, L. *Org. Biomol. Chem.* **2004**, *2*, 1582–1586.
22. (a) Kumagai, H.; Hasegawa, M.; Miyanari, S.; Sugawa, Y.; Sato, Y.; Hori, T.; Ueda, S.; Kameyama, H.; Miyano, S. *Tetrahedron Lett.* **1997**, *38*, 3971–3972.
23. (a) Iki, N.; Miyano, S. *J. Inclusion Phenom.* **2001**, *41*, 99–105; (b) Morohashi, N.; Narumi, F.; Iki, N.; Hattori, T.; Miyano, S. *Chem. Rev.* **2006**, *106*, 5291–5316; (c) Shokova, E. A.; Kovalev, V. V. *Russ. J. Org. Chem.* **2003**, *39*, 1–28; (d) Hu, X.; Xia, N.; Ye, F.; Ren, J.; Shi, X. *Spectrochim. Acta, Part A* **2004**, *60*, 1427–1430; (e) Lhotak, P. *Eur. J. Org. Chem.* **2004**, 1675–1692.
24. (a) Lhotak, P.; Svoboda, J.; Stibor, I. *Tetrahedron* **2006**, *62*, 1253–1257; (b) Lang, K.; Curinova, P.; Dudic, M.; Proskova, P.; Stibor, I.; St'astny, V.; Lhotak, P. *Tetrahedron Lett.* **2005**, *46*, 4469–4472; (c) Zlaatuskova, P.; Stibor, I.; Tkadlecova, M.; Lhotak, P. *Tetrahedron* **2004**, *60*, 11383–11390.
25. (a) Dhir, A.; Bhalla, V.; Kumar, M. *Org. Lett.* **2008**, *10*, 4891–4894; (b) Kumar, R.; Bhalla, V.; Kumar, M. *Tetrahedron* **2008**, *64*, 8095–8101; (c) Mahajan, R. K.; Kaur, R.; Bhalla, V.; Kumar, M.; Hattori, T.; Miyano, S. *Sens. Actuators, B* **2008**, *130*, 290–294; (d) Bhalla, V.; Babu, J. N.; Kumar, M.; Hattori, T.; Miyano, S. *Tetrahedron Lett.* **2007**, *48*, 1581–1585; (e) Bhalla, V.; Kumar, M.; Katagiri, H.; Hattori, T.; Miyano, S. *Tetrahedron Lett.* **2005**, *46*, 121–124; (f) Kumar, M.; Sharma (nee Bhalla), V.; Babu, J. N. *Tetrahedron* **2003**, *59*, 3267–3273.
26. (a) Babu, J. N.; Bhalla, V.; Kumar, M.; Puri, R. K.; Mahajan, R. K. *New J. Chem.* **2009**, *33*, 675–681; (b) Babu, J. N.; Bhalla, V.; Kumar, M.; Mahajan, R. K.; Puri, R. K. *Tetrahedron Lett.* **2008**, *49*, 2772–2775; (c) Babu, J. N.; Bhalla, V.; Kumar, M.; Singh, H. *Lett. Org. Chem.* **2006**, *3*, 787–793.
27. Long, G. L.; Winefordner, J. D. *Anal. Chem.* **1983**, *55*, 712A–714A.
28. Jung, H. S.; Kim, H. J.; Vicens, J.; Kim, J. S. *Tetrahedron Lett.* **2009**, *50*, 983–987.
29. (a) Xie, H.; Yi, S.; Yang, X.; Wu, S. *New J. Chem.* **1999**, *23*, 1105–1110; (b) Bernardo, M. A.; Alves, S.; Pina, F.; De Melo, J. S.; Albelda, M. T.; Garcia-España, E.; Llinares, J. M.; Soriano, C.; Luis, S. V. *Supramol. Chem.* **2001**, *13*, 435–445; (c) Albelda, M. T.; Bernardo, M. A.; Diaz, P.; García-España, E.; de Melo, J. S.; Pina, F.; Soriano, C.; Luis, S. V. *Chem. Commun.* **2001**, 1520–1521; (d) de Melo, J. S.; Albelda, M. T.; Diaz, P.; García-España, E.; Lodeiro, C.; Alves, S.; Lima, J. C.; Pina, F.; Soriano, C. *J. Chem. Soc., Perkin Trans. 2* **2002**, 991–998; (e) Mei, M.; Wu, S. *New J. Chem.* **2001**, *25*, 471–475; (f) Lin, Z. H.; Xie, L. X.; Zhao, Y. G.; Duan, C. Y.; Qu, J. P. *Org. Biomol. Chem.* **2007**, *5*, 3535–3538.
30. Gampp, H.; Maeder, M.; Meyer, C. J.; Zuberbulher, A. D. *Talanta* **1985**, *32*, 95–101.