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Calixarene-Derived Fluorescent Probes

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Contents

1. Introduction

Cations and anions play an important role in a wide range of chemical reactions, including biological metabolism as well as many other processes.[1−6] For the purpose of detection and quantitative determination of ions, much effort has been devoted to the development of appropriate chemosensors.[7−18] The main issue in the design of any effective chemosensor is the association of a selective molecular recognition event with a physical signal highly sensitive to its occurrence. Changes in both the absorption and emission of light can be utilized as signals provided appropriate chromophores or fluorophores are available, and two important classes of sensors are those of the optical and fluorimetric types. While spectrophotometry and fluorimetry are both relatively simple techniques which are rapidly performed, nondestructive and suited to multicomponent analysis, fluorimetry is commonly considered superior, principally because of its greater sensitivity.[7,19−23] Whereas absorbance measurements can at best determine concentrations down to ~0.1 μM, fluorescence techniques can accurately measure concentrations 1 million times smaller. An additional advantage of fluorimetry is that discrimination between analytes is possible by time-resolved measurements.[24] In general, for fluorimetric determination of cations or anions, any sensor must include two components, an ionophore and a fluorophore, which can be independent species or covalently linked in one molecule.[25,26] The ionophore is required for selective binding of the substrate, while the fluorophore provides the means of signaling this binding, whether by fluorescence enhancement or inhibition. Mechanisms which control the response of a fluorophore to substrate binding include photoinduced electron transfer (PET),[27−33] Fluorescence (Förster) resonance energy transfer (FRET),[34−36] excimer/exciplex formation or extinction,[27,37] and photoinduced charge transfer (PCT).[38−45]

The cyclooligomeric phenols known as calixarenes have received much interest as basic molecular scaffolds for the construction of selective ionophores, many of which have been incorporated into fluorescent ion sensors.[1,10,19,28−32,38,46−54] Though the chemistry of calixarenes can be traced back to Bayer's 19th-century investigations of phenol/formaldehyde reactions, it was the clarification of their nature and development of efficient syntheses, largely due to Gutsche et al. in the 1970s,[55−57] that produced an intense development of this field, now comprehensively detailed in numerous books.[38,40,58−63] In this review, the focus is upon derivatives of the four conformational isomers, cone, partial-cone, 1,2-alternate, and 1,3-alternate, of calix[4]arene in particular.[38,40,64−66] While studies of calix[4]arene derivatives still define the bulk of the literature concerning calixarenes, it may be noted that, aside from homologues of calix[4]arene, there are also important groups of related macrocycles such as the homocalixarenes,[67] the homooxacalixarenes,[68,69] the thiacalixarenes,[70−73] the homothiacalixarenes,[74] the homoazacalixarenes (or azacalixarenes),[75−80a] and the resorcinarenes,[80b−d] where the methylene group of the "normal" calixarene is replaced by various other units. There are also rather more remotely related macrocycles such as the calixpyrroles, which have been extensively studied for their anion-binding properties.[80e] These may well provide a basis for further developments in sensor chemistry, but the focus of the present review is essentially on calix[4]arene-based ion sensor developments over the past decade, with a particular emphasis upon analysis of the photophysical mechanisms which determine sensor properties.

2. Photophysics of Fluorescent Sensors

2.1. Photoinduced Electron Transfer

In the simplest cases, emission of a photon, fluorescence, follows HOMO to LUMO excitation of an electron in a molecule. Where this emission is efficient, the molecule may be termed a fluorophore. Vibrational deactivation of the excited state prior to emission usually gives rise to a "Stokes shift" in that the wavelength of the emitted radiation is less than that of the exciting radiation.[81] Various other interactions may also modify the emission process, and these are of considerable importance in regard to analytical applications of fluorescence.

Thus, when a lone electron pair is located in an orbital of the fluorophore itself or an adjacent molecule and the energy

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Duong Tuan Quang was born in 1970 in Thanhhoa, Vietnam, and graduated from Hue University in 1992, where he obtained his M.S. degree 2 years later and began his career as a lecturer in chemistry soon afterward. He received his Ph.D. degree in 2003 from the Institute of Chemistry, Vietnamese Academy of Science and Technology, for research on platinum(II) complexes of thiosemicarbazone derivatives supervised by Prof. Chu Dinh Kinh and Prof. Vu Dang Do. In 2006, he worked as a postdoctoral fellow in Prof. Jong Seung Kim's laboratory, Department of Chemistry, Dankook University, Seoul, Korea. His main task involved the development of chromogenic and fluorogenic chemosensors to detect specific cations, anions, and neutral molecules.

of this orbital lies between those of the HOMO and LUMO, efficient electron transfer of one electron of the pair to the hole in the HOMO created by light absorption may occur, followed by transfer of the initially excited electron to the lone pair orbital. Such PET provides a mechanism for nonradiative deactivation of the excited state (Figure 1), leading to a decrease in emission intensity or "quenching" of the fluorescence.[7,29,30,32,82]

Fluorescence lost as a result of PET may be recovered if it is possible to involve the lone pair in a bonding interaction. Thus, protonation or binding of a metal ion effectively places the electron pair in an orbital of lower energy and inhibits the electron-transfer process. The excited-state energy may then again be lost by radiative emission. In the case of metal ion binding, this effect is referred to as chelation-enhanced fluorescence (CHEF).[10,46b,47]

In some cases, complexation of metal ions, Cu(II) and Ni(II), for example,[83−86] does not induce CHEF but causes the fluorescence to be quenched via two well-defined mechanisms, electron transfer (eT) and energy transfer (ET) to the metal ion, that lead to rapid nonradiative decay. While the ET process (Figure 2) involves no formal charge transfer, the eT process does and must therefore be associated with some spatial reorganization of solvating molecules, so that inhibition of their motions should cause inhibition of eT. Thus, the two processes can be distinguished by comparing the luminescence of liquid and frozen solutions, enhancement of luminescence in the latter indicating that eT must be responsible for quenching in the liquid solution. It has been shown that eT has a weaker dependence on the donor−acceptor separation than ET, so that eT tends to dominate for longer separations and ET for shorter.[87,88]

2.2. Excimer Formation

Where aromatic rings are involved in weak interactions (such as π-stacking) which bring them within van der Waals contact distances, electronic excitation of one ring can cause an enhanced interaction with its neighbor, leading to what is termed an excited-state dimer or "excimer".[89,90] In other words, an excimer is a complex formed by the interaction of an excited fluorophore with another fluorophore in its ground state. Excimer emission typically provides a broad fluorescence band without vibrational structure, with the maximum shifted, in the case of most aromatic molecules,[91] by about 6000 cm^{-1} to lower energies compared to that of the uncomplexed ("monomer") fluorophore emission. An excimer may also form from an excited monomer if the interaction develops within the lifetime of the latter. Thus, it is expected that excimers are more likely to be produced by relatively long-lived monomer excited states.[92−95] Rates of fluorophore diffusion, especially in viscous solvents, are therefore another limit on excimer formation.[96−99] Importantly, the separation and relative orientation of multiple fluorophore units attached to ligands can be controlled by metal ion coordination, so that recognition of a cation can be monitored by the monomer:excimer fluorescence intensity ratio.[7,93,89,100,101]

2.3. Photoinduced Charge Transfer

Electronic excitation necessarily involves some degree of charge transfer, but in fluorophores containing both electron-withdrawing and electron-donating substituents, this charge transfer may occur over long distances and be associated with major dipole moment changes, making the process particularly sensitive to the microenvironment of the fluorophore. Thus, it can be expected that cations or anions in close interaction with the donor or the acceptor moiety will change the photophysical properties of the fluorophore.[1,20,102]

Upon, for example, cation complexation of an electron donor group within a fluorophore, the electron-donating

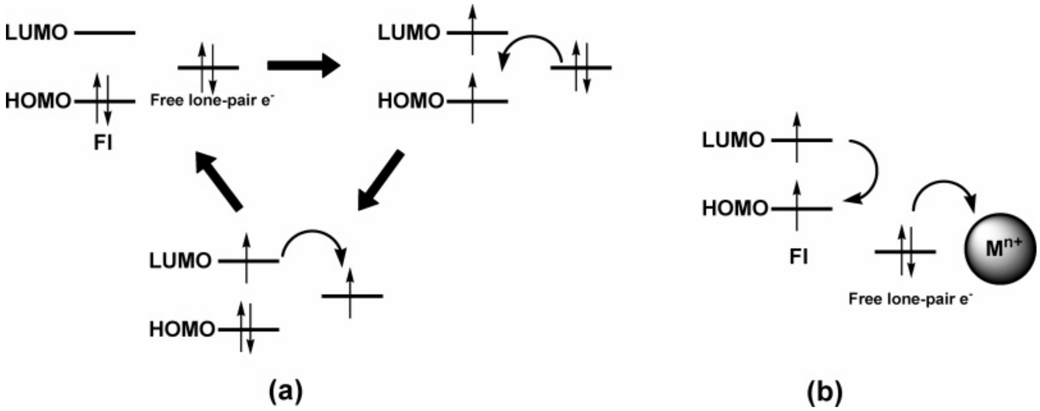


Figure 1. Mechanisms for PET (a) and CHEF (b) systems.

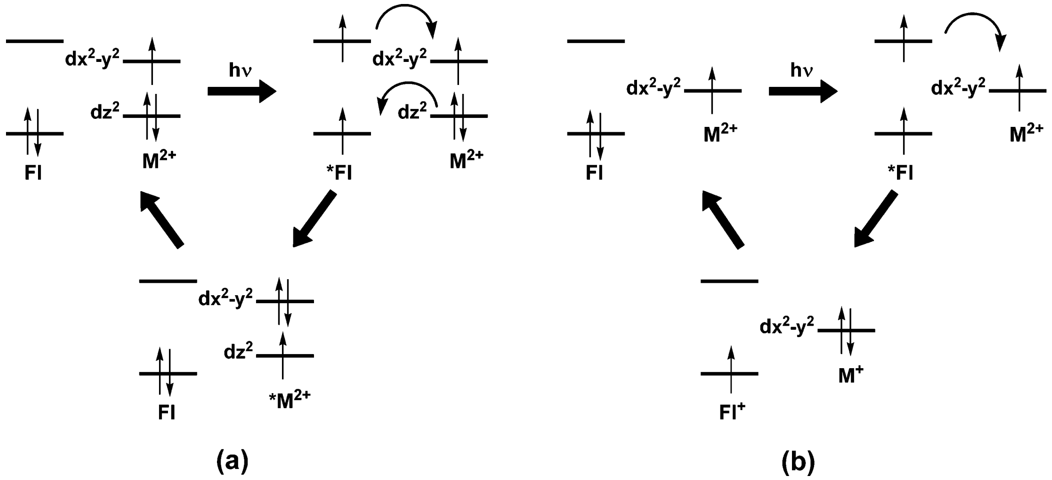


Figure 2. Mechanisms for (a) ET and (b) eT in systems containing an excited fluorophore and a d^9 metal ion.

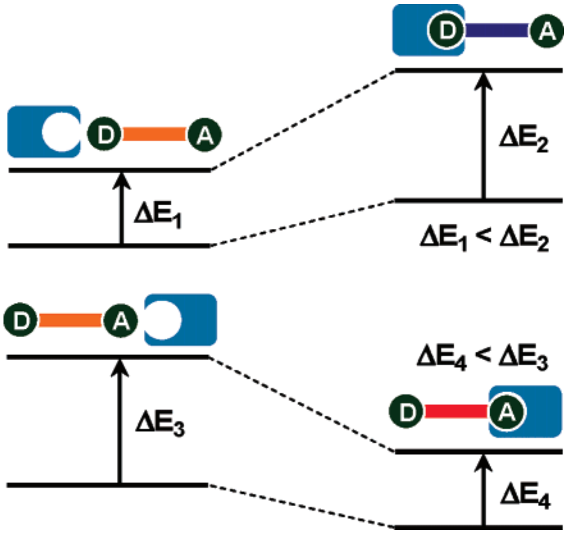


Figure 3. PCT system.

character of the donor group will be reduced. The resulting reduction of conjugation causes a blue shift of the absorption spectrum together with a decrease of the molar absorptivity. In contrast, metal ion binding to the acceptor group enhances its electron-withdrawing character, and the absorption spectrum is thus red-shifted with an increase in molar absorptivity (see Figure 3).[103] The fluorescence spectra should be shifted in the same direction as the absorption spectra, and in addition to these shifts, changes in the quantum yields and lifetimes can be observed. All these photophysical effects are obviously dependent on the charge and the size of the cation, and therefore, some selectivity is expected.[104]

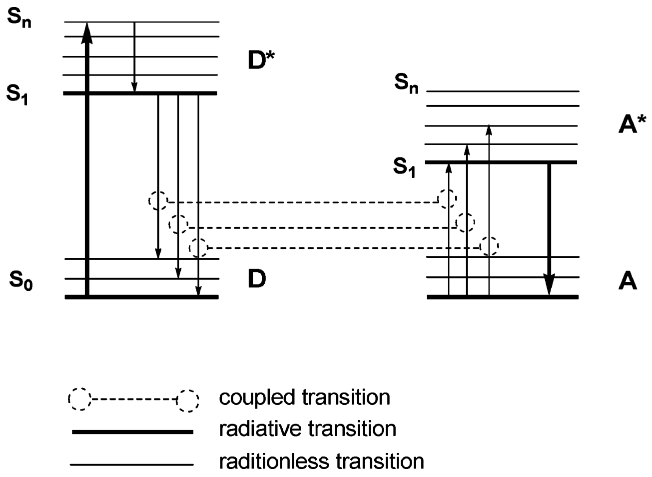


Figure 4. Fluorescence (Förster) resonance energy transfer system.

2.4. Fluorescence Resonance Energy Transfer

FRET arises from an interaction between a pair of dissimilar fluorophores in which one acts as a donor of excited-state energy to the other (acceptor). This returns the donor to its electronic ground state, and emission may then occur from the acceptor center (see Figure 4). FRET is influenced by three factors: the distance between the donor and the acceptor, the extent of spectral overlap between the donor emission and acceptor absorption spectrum (see Figure

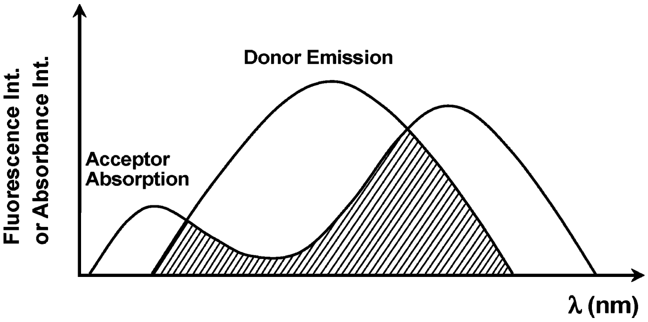


Figure 5. Spectral overlap for FRET.

5), and the relative orientation of the donor emission dipole moment and acceptor absorption moment.[81,105]

3. Calixarene-Based Fluorescent Sensors

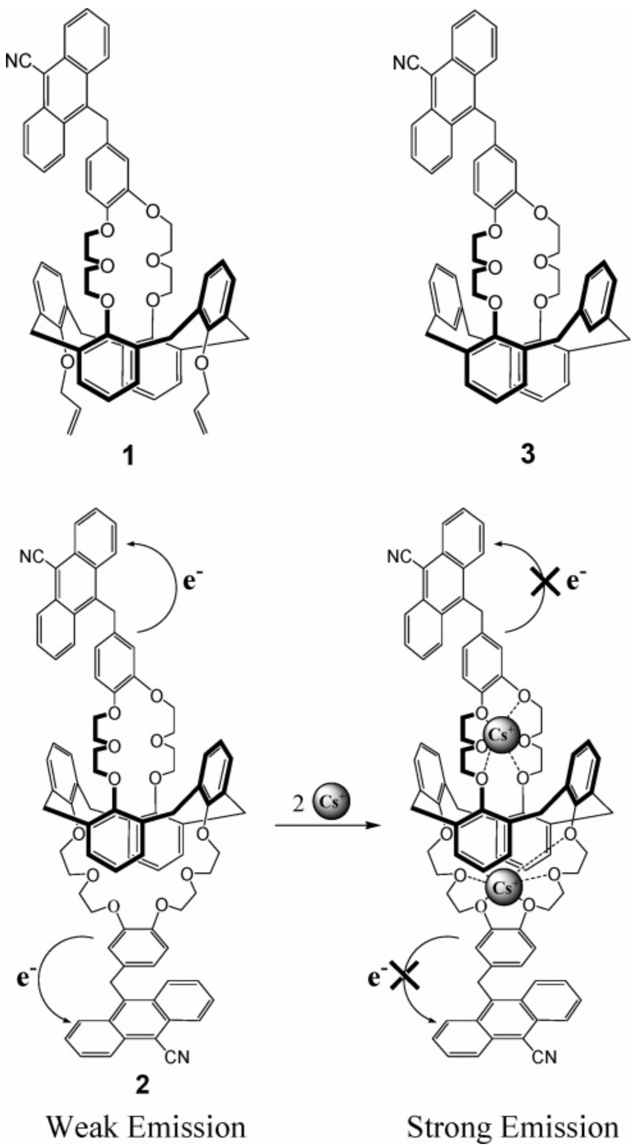
3.1. PET Sensors

In an effort to develop a technique for Cs$^+$ determination, **1** and **2** were prepared and studied by Ji et al.[31,32] When excited at 320 nm, they show two emissions at ca. 430 and ca. 450 nm. In the absence of metal ion, their fluorescence is weak due to the PET from the oxygen atoms of the benzo moiety to the excited singlet state of the cyanoanthracene fluorophore. The maximum enhancements in the emission of **1** and **2** (Chart 1) in CH_2Cl_2/CH_3OH (1:1, v/v) upon the addition of Cs$^+$ are 8.2- and 11.7-fold, respectively. These enhancements can be explained by the fact that complexation of the oxygen atoms by Cs$^+$ inhibits PET, i.e., that there is a CHEF effect.[46b,c,47] It is probable (see ahead) that larger effects might be observed where a more strongly reducing amino substituent is the cause of the PET.[7,10] In the presence of a large excess of Cs$^+$ (up to (3.0×10^4)-fold), the emission intensity is reduced, attributed by the authors to the increased polarity of the medium favoring the PET process.

Compound **3**,[30] with the same fluorophore as **1** but based on a slightly different calixarene platform, shows not only an increased selectivity toward Cs$^+$ but also a remarkable enhancement in the fluorescent emission intensity by Cs$^+$ compared with the other systems. Even addition of only a small amount of Cs$^+$ (1.0×10^{-7} M) to **3** (10^{-6} M) in CH_2Cl_2/CH_3OH (1:1, v/v) leads to a 20-fold fluorescent emission enhancement, while there is no detectable response to other alkali-metal ions except Rb$^+$ (2-fold enhancement) at the same concentration. When fully complexed by Cs$^+$, the fluorescence quantum yield of **3** is 54 times greater than that of the free ligand.

Calix[4]arenes **4** and **5** (Chart 2), quite different from **1**−**3** in the composition of the crown moiety,[106] have one or two anthracene fluorophores directly attached to the nitrogen atom of a 1,3-alternate calix[4]azacrown-6. Their weak emission is inhibited by PET from the nitrogen lone pair electrons to the excited singlet state of the anthracene fluorophore. The addition of Cs$^+$ to **4** and **5** in CH_2Cl_2/CH_3OH (1:1, v/v) causes 8.5-fold and 11.6-fold enhancements, respectively, indicating that the N atom is coordinated by Cs$^+$, reducing its ability to participate in PET. However, the Cs$^+$:K$^+$ selectivity ratios for **4** and **5** are 22.3 and 18.0, respectively, which are lower than the values reported for some other calixarenes.

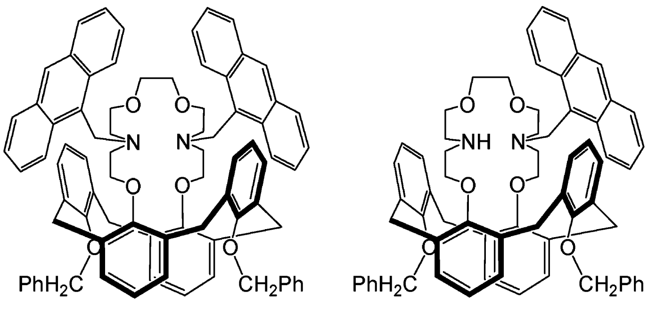
Chart 1



1 **3**

2

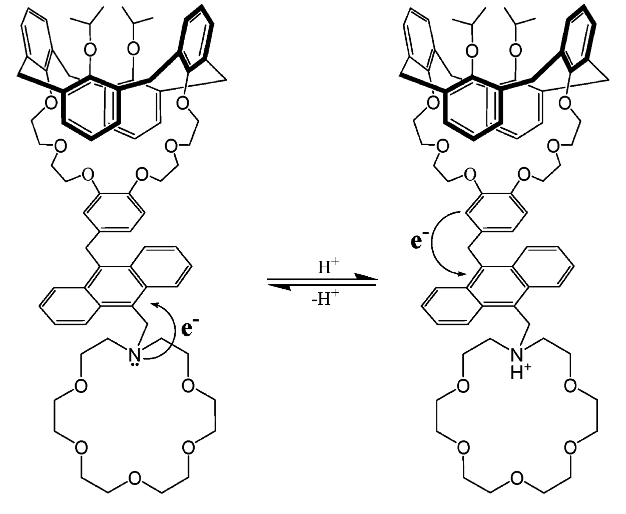
Chart 2



4 **5**

Ji et al. also reported that **6** (Chart 3),[107] possessing a single fluorophore, is influenced by two different binding sites. In basic CH_3OH, **6** shows a weak emission due to the quenching of anthracene fluorescence by PET involving the lone pair electrons of the N atom of the azacrown ring. In acidic medium, this lone pair is protonated, but PET quenching of the fluorophore still occurs through the dialkoxybenzene moiety. This in turn can be inhibited by cation coordination, and **6** is highly sensitive to Cs$^+$ over other alkali-metal ions in acidic medium, up to a 3.8-fold enhancement of emission intensity being observed. In a basic medium, selective binding of K$^+$ to the azacrown leads to a maximum 6.4-fold emission enhancement, and for this reason, **6** can be used as

Chart 3



6

a dual sensor for detection of both Cs^+ and K^+ in the same solution.

Calixarene **7**[29] (Chart 4) bearing four carbonyl functions, two of them being linked to pyrene and nitrobenzene at opposite sites on the lower rim, was prepared for Na^+ sensing. As the free ligand, **7** shows fluorescence similar to that of **8**,[29] but its intensity is 50 times weaker, suggesting that the fluorescence quenching in **7** is due to intramolecular PET between the nitrobenzyl acceptor and excited pyrene fluorophore, a conclusion supported by the fact that the fluorescence is not solvent sensitive. Binding of Na^+ to **7** in diethyl ether appears to cause a conformational change where the nitrobenzyl and pyrenyl substituents become more distant, leading to reduced PET seen as an enhancement in the fluorescence quantum yield from 0.0025 to 0.016.

PET-based fluorescent changes of calixarenes have been widely studied by Kim et al. The luminescence of **9**[47] (Chart 5) was reported to be partially quenched by PET from the azacrown ring to the pyrenyl unit. On complexation with K^+, Rb^+, Cu^{2+}, and Pb^{2+} in ethanol, the fluorescence of **9** is considerably enhanced by a CHEF effect due to the coordination of the lone pair on N by the metal ions inhibiting PET. Binding of Cu^{2+} or Pb^{2+} leads to a maximum 50-fold intensity enhancement, whereas Rb^+ and K^+ cause 12- and 10-fold enhancements, respectively. The CHEF effects of Ag^+ and Co^{2+} are rather small, and that of Na^+ is negligible.

In contrast, calixarene **10** (Chart 6) bearing a crown ether and an azacrown ether as two binding sites displays similar CHEF effects for Ag^+, Co^{2+}, Cu^{2+}, and Pb^{2+}.[47] Unlike **9**, **10** does not show any CHEF upon addition of K^+ and Rb^+. This is attributed to preferential binding of the alkali-metal ions to the crown ring and the other metal ions to the azacrown unit, only the latter resulting in a significant inhibition of PET.

Similar observations have been made with **10**, for which the fluorescence in ethanol is almost completely quenched by PET. Binding of Ag^+ produces a CHEF effect due to its coordination at the N atom, but addition of K^+ to this complex causes fluorescence quenching due to its preferential binding in the crown loop, which causes ejection of Ag^+ from the azacrown entity. This "entry-ejection" process has been termed "molecular taekwondo", and it is readily monitored by fluorescence changes. It has also been observed with the $Cu^{2+}-K^+$ pair, but owing to the major difference in stability constant values, a decrease in fluorescence emission can only be observed when excess K^+ is added to an ethanolic solution of **10** in the presence of 1 equiv of Cu^{2+}.

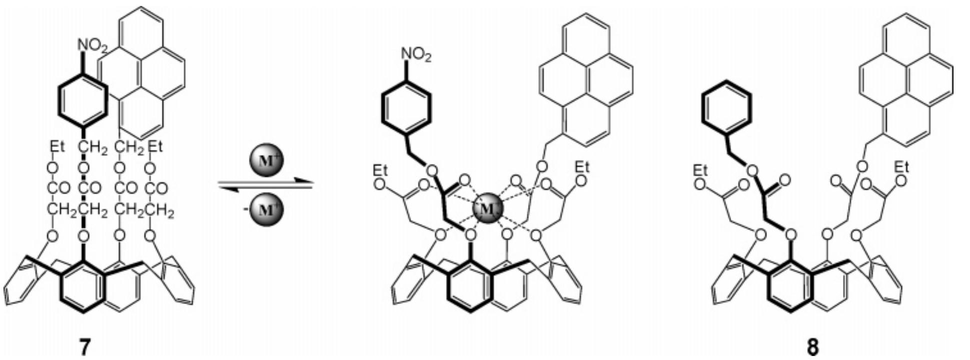
An interesting process related to the action of a "molecular syringe"[46a] and presumably involving cation tunneling through the π-basic calixtube[108] is observed upon the addition of CF_3COOH to **10**$\cdot Ag^+$[47] in C_2H_5OH/CH_2Cl_2 (9:1, v/v) and gives rise to a further enhancement in fluorescence intensity. Here, protonation of the azacrown forces the Ag^+ to migrate to the less preferred crown site.

The replacement of the crown-5 ether in **10** by the crown-6 ether, which is a suitable cavity for Cs^+, leads to **11** (Chart 7).[47] Again, complexation of Ag^+ in the azacrown unit causes an enhancement in fluorescence emission due to the CHEF effect, and now addition of Cs^+ to **11**$\cdot Ag^+$ in ethanol ejects Ag^+, causing fluorescence quenching, but addition of K^+ does not. This can be explained as due to the preferential binding of Cs^+ over K^+ by the calixcrown-6 site.

Calix[4]azacrown **12**[46] (Chart 8), bearing an anthracenyl unit, was reported to have a pronounced CHEF effect with Cs^+, Rb^+, and K^+ ions. In this case, the anthracenyl fluorophore is bound to the crown site, in contrast to the situation in **11** where the pyrenyl fluorophore is attached to the azacrown site. Thus, an inverse "taekwondo" process is observed compared to that for **11**. The addition of Cu^{2+} to an C_2H_5OH/CH_2Cl_2 solution containing the complex **12**$\cdot Cs^+$ causes fluorescence quenching due to binding of Cu^{2+} to the azacrown ether, which causes ejection of Cs^+ and thus facilitates PET between the proximate crown oxygen atoms and the excited anthracenyl. Similar effects are seen with Ag^+ in place of Cu^{2+}.

Compounds **13** and **14** (Chart 9), containing two pyrene moieties and a pendent primary alkylamine, provide systems where both monomer and excimer emissions may be affected

Chart 4



7 **8**

Chart 5

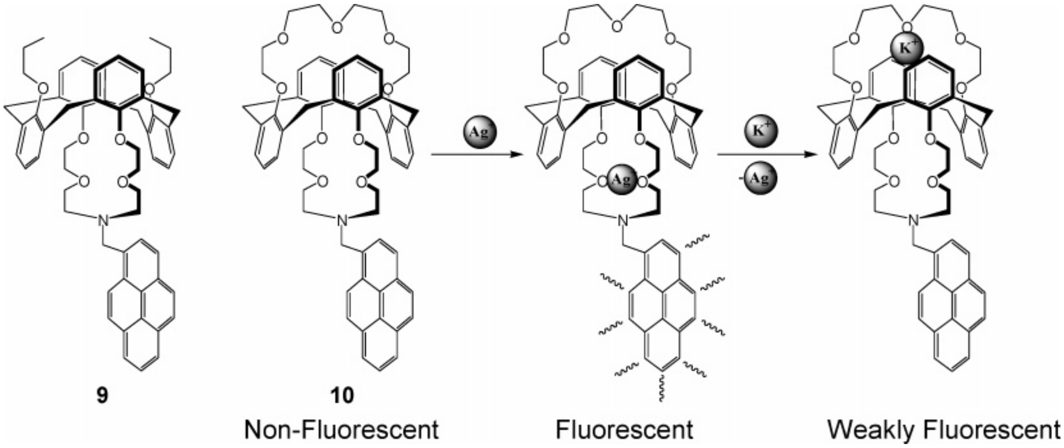


Chart 6

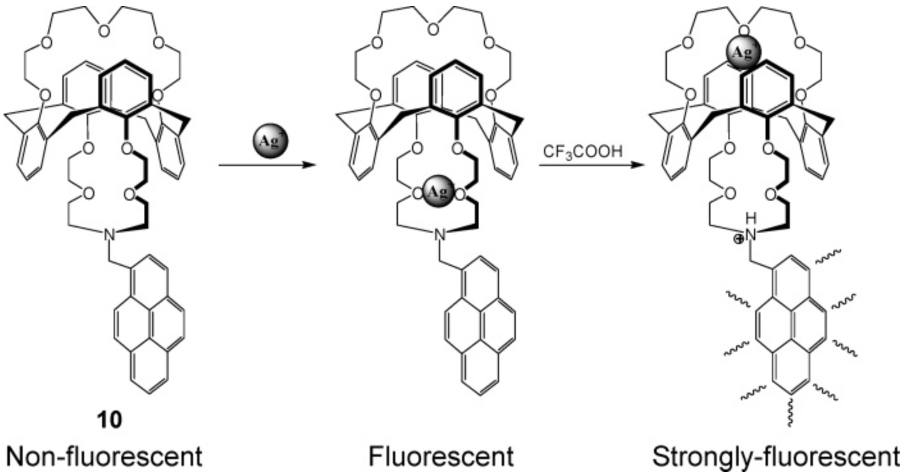
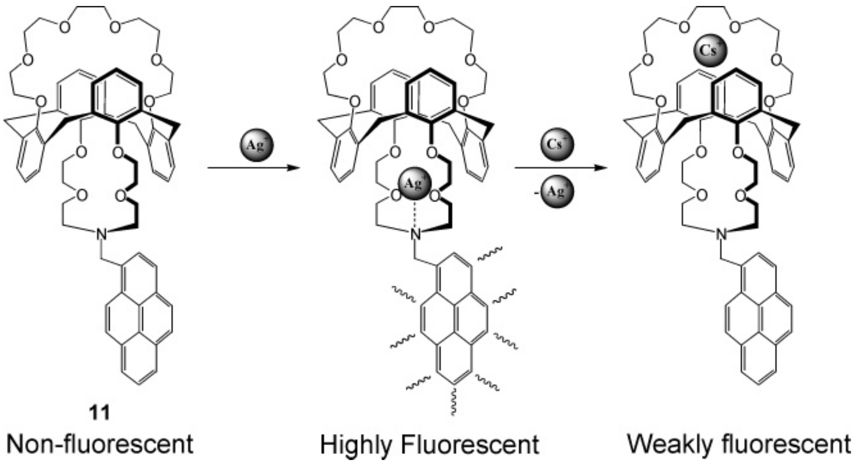


Chart 7



by PET.[94] That their weak emission is a consequence of PET is confirmed by a comparison with **15**, a calixarene having the same structure as **13** but without an attached amine group, where strong monomer and excimer emissions are seen. In the presence of Pb^{2+}, both **13** and **14** in CH_3CN exhibit an enhanced monomer emission and diminished excimer emission. This CHEF effect can be attributed to a conformational change due to the metal binding as well as to the coordination of the electron-donor N center. However, upon addition of alkali-metal ions to **13** and **14**, both monomer and excimer emissions are enhanced, suggesting that there is no conformational change involved. A competitive metal ion exchange experiment shows that the binding ability of **13** for Pb^{2+} is much greater than that for Li^+.

Kim et al. also reported the synthesis and study of **16** and **17** (Chart 10),[109] in which a (bromoanthracenyl)methyl unit is directly attached to the nitrogen atom of a 1,3-alternate calix[4]azacrown-6. Their composition is not much different from that of **4** and **5**, although they are not selective for alkali-metal ions but instead for In^{3+} and Pb^{2+} in C_2H_5OH or $ClCH_2CH_2Cl/CH_3CN$ (1:1, v/v). Emission from **17** is 20 times more sensitive to In(III) addition than that from **16**, indicating that conformational differences may influence quenching by PET.

Chart 8

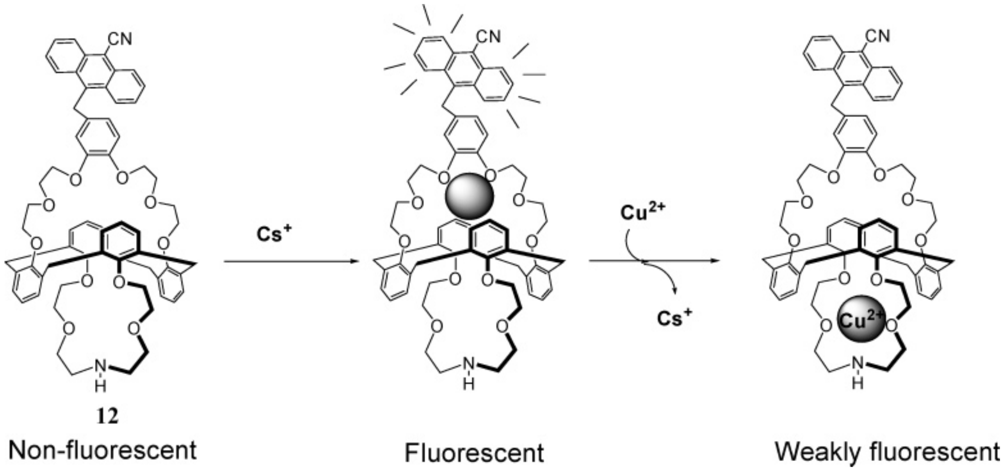
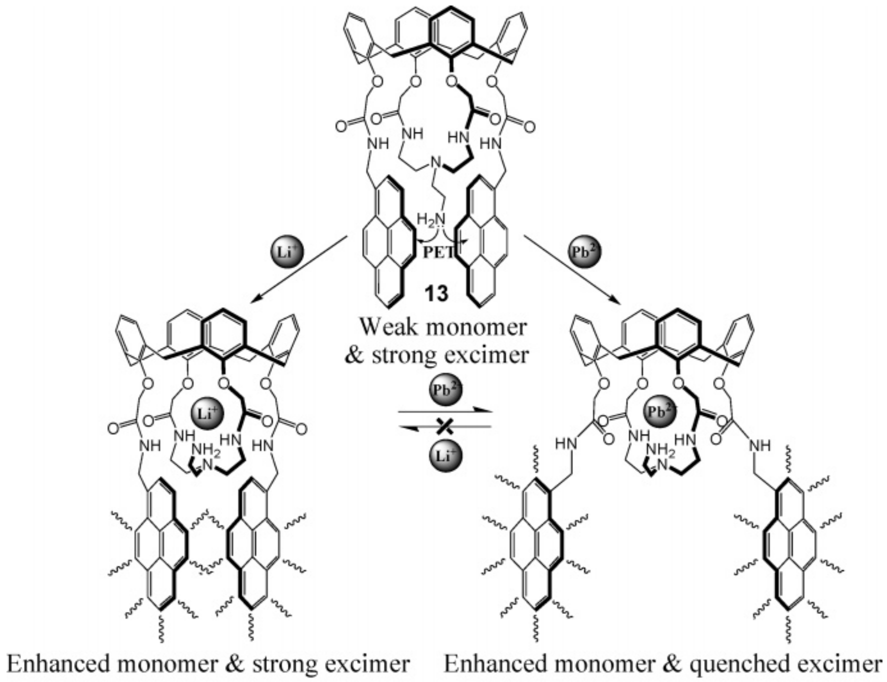
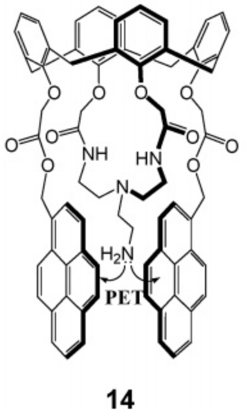


Chart 9





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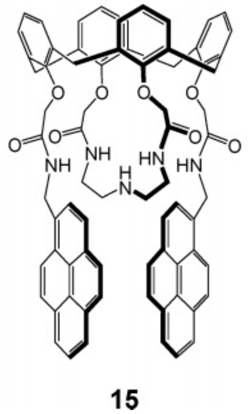
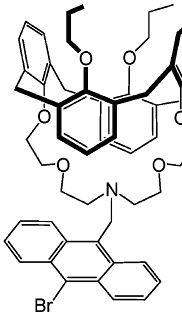


15

Crown-5 loops within a 1,3-alternate calix[4]biscrown are expected to be favorable sites for K^+ binding.[110,111] Recently, Kim et al. synthesized **18** (Chart 11), bearing such a loop, showing a high selectivity for K^+ in CH_3CN.[112] Without the presence of metal ion, **18** exhibits a relatively weak fluorescence in comparison with **19**, indicating PET involving both the benzene rings of the calix[4]arene and the oxygen atoms of the crown-5 ring. The fluorescence of **18** is greatly increased upon the addition of K^+, whereas that of **19** remains almost unchanged, suggesting that this ion prefers binding to the crown-5 than to the 1,5-naphthalene crown-6 site. Binding of Pb^{2+} caused luminescence quench-

Chart 10



16

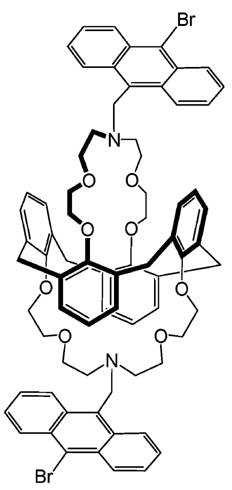


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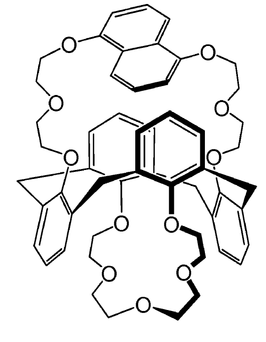
Chart 11



18

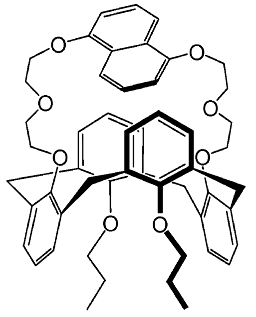


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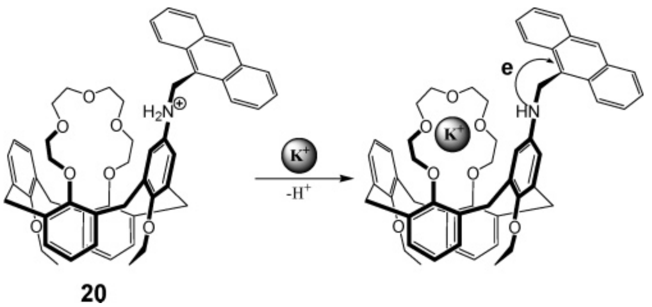
Chart 12



20

ing, much greater in the case of **18** than **19**, thus again indicating the crown-5 site to be the more effective metal-binding entity.

Like metal ions, H^+ may bind to an electron-donor site such as N, and thus, the emission from **20** (Chart 12) is much stronger in acidic than in neutral or basic solutions due to the inhibition of PET. However, complexation of K^+ in CH_3CN/H_2O (9:1, v/v) acidified with 1.0×10^{-2} M HCl leads to a diminished basicity at N and hence to a reduced degree of protonation and a weaker luminescence.[113]

Fluorescence quenching commonly occurs by the PET mechanism described above in which the excited state acts as an oxidant, although the inverse phenomenon, termed reverse PET, is also sometimes observed. Thus, **21** (Chart 13) exhibits a strong emission at ca. 400 nm when excited at 344 nm.[114] Addition of Pb^{2+} to **21** in $CH_3CN/CHCl_3$ (1:1, v/v) causes a marked decrease in fluorescence intensity, attributed to reverse PET involving electron donation from the excited pyrene unit to the carbonyl groups, the electron density of which is decreased by Pb^{2+} complexation. A "heavy metal effect" due to the redox activity of the metal ion cannot, however, be excluded.

Like **21**, **22**[115] (Chart 14) also bears two pyrene amide moieties and a crown-5 ether unit and therefore exhibits nearly the same fluorescence behavior and quenching mechanism upon complexation of Pb^{2+} in CH_3CN. In contrast, **23**[115] bearing a crown-5 unit is not selective for this ion because binding within the relatiely small macrocyclic ring sterically restricts interactions with the amide carbonyl oxygen atoms. Replacement of the crown-5 in **22** by azacrown-5 gives **24**,[95] which is also selective for Pb^{2+}. The quenching in this case probably results from a combination of reverse PET, the heavy metal effect, and a conformational change.

The anthracene-based fluorescent calix[4]arene **25** (Chart 15) studied by Vicens et al.[83] shows a high selectivity for transition-metal ions such as Zn^{2+} and Ni^{2+} in CH_3CN/H_2O (4:1, v/v). Complexation of Zn^{2+} prevents PET quenching by the amine N donors, and since Zn(II) is redox-inactive and has no low-lying electronic states, no "heavy-metal effect" occurs, so fluorescence is enhanced. Complexation of Ni^{2+} causes the excited fluorophore anthracenyl to be deactivated through a double electron exchange (ET process of the Dexter type; see the scheme below) involving the highest occupied d orbitals of this ion and giving a quenching of fluorescence.[87]

Very similar behavior was also seen in the study by Y.-D. Cao et al.[116] showing that **26** can be used as a fluorescent chemosensor for Cu^{2+} and Zn^{2+} in CH_3OH/H_2O (9:1, v/v) with pH control.[116] When excited at 340 nm, free **26** (Chart 16) shows a weak emission at 408 nm due to the PET between the imidazoles and the fluorophore. When protonated, the PET process is suppressed to give an increased fluorescence. While Cu(II) coordination could be expected to produce a CHEF effect, in its complex with **26** there is an eT between Cu^{2+} and the excited fluorophore which dominates and leads to quenching. As expected, the eT pathway is not available for Zn(II), so the CHEF effect operates and the emission intensity is greater. Other cations tested gave negligible effects due to their weak complexation. The fluorescence changes induced by Cu^{2+} and Zn^{2+} are most apparent in a medium of pH 10.

Fluorescence quenching by PET processes involving an eT mechanism was also reported in the cases of **27**,[117] **28**,[118] and **29** (Chart 17).[119a] Incorporating dansyl fluorophore moieties into a calix[4]arene bis(*N*-X-sulfonyl carboxamide) leads to **27**, which is the first example of a Hg(II)-selective fluorescent calixarene. Addition of Hg^{2+} to **27** in $CHCl_3$ causes fluorescence to be quenched due to electron transfer from the excited dansyl moiety to Hg^{2+}. The presence of alkali-, alkaline-earth-, and transition-metal ions does not affect the quenching of **27** induced by Hg^{2+}. In CH_3CN/H_2O (1:1, v/v), Hg^{2+} binding to **28**, bearing dansyl amide positioned at the nitrogen atom of an azacrown moiety, is also selective and produces similar fluorescence quenching. **29**, derived from a calixarene bearing two 3-alkoxy-2-naphthoic acid moieties, shows a high selectivity for Cu^{2+} and Fe^{3+} with pH control. The deprotonated oxygen atom of the electron-rich carboxylate is most strongly bound to Cu^{2+} at pH ca. 7 and to Fe^{3+} at pH ca. 5.5 in CH_3OH/H_2O (1:1, v/v), leading to strong fluorescence quenching induced by eT from the excited naphthalene moiety to these cations. At higher pH, the two phenol groups of calixarene are

Chart 13

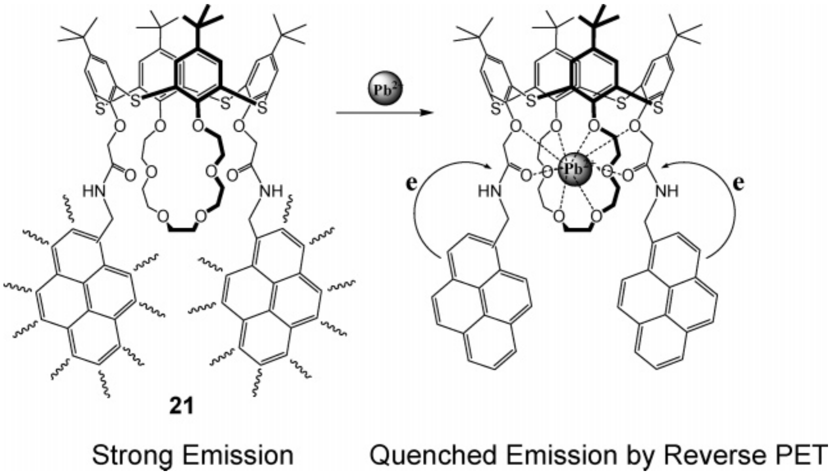
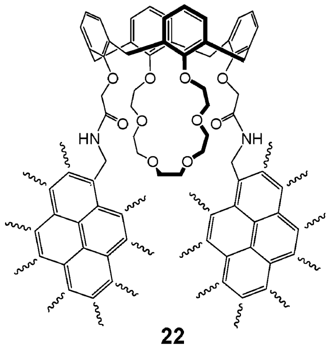


Chart 14



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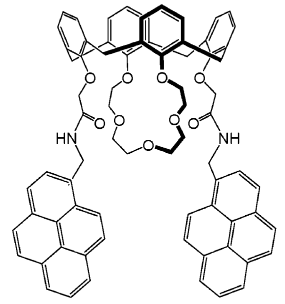

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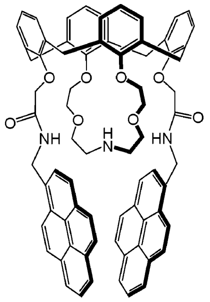
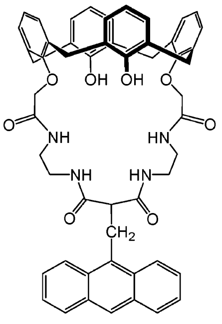


24

Chart 15



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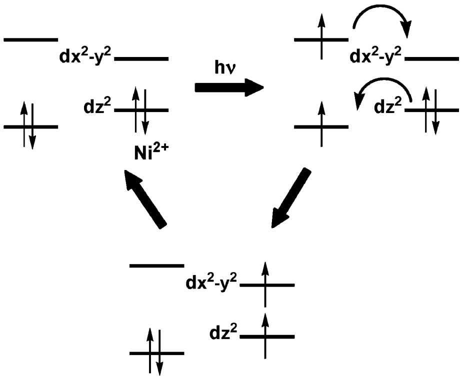
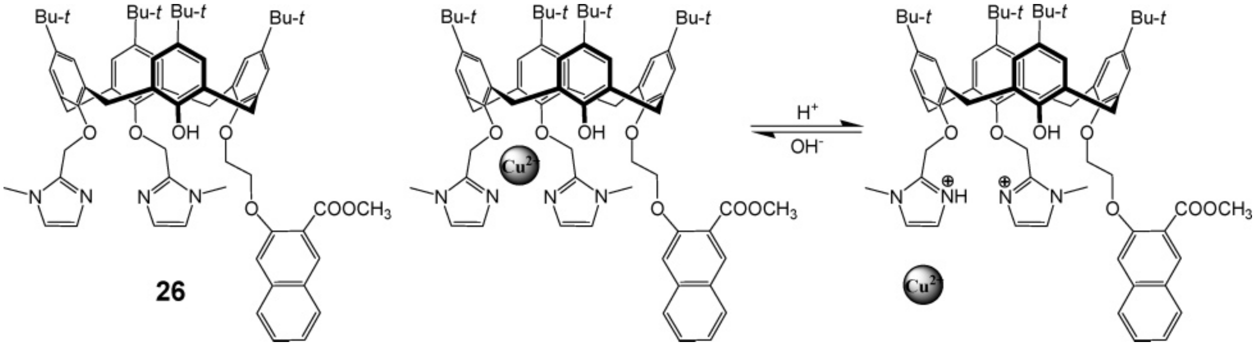


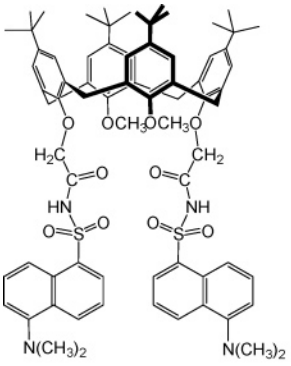
Chart 16



deprotonated, and the cations move to the calixarene cavity due to their stronger complexation with the phenolic oxygen atom, so that eT no longer occurs and fluorescence enhancement is observed.

A calixarene-based fluoroionophore, **30** (Chart 18),[119b] grafted on SBA-15 mesostructured silica can be used to detect Hg^{2+} ion in aqueous media. A rapid response of only a few seconds is observed, and Hg(II) complexation induces

Chart 17



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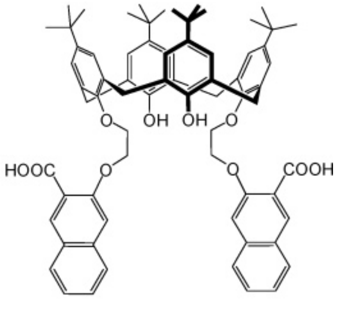

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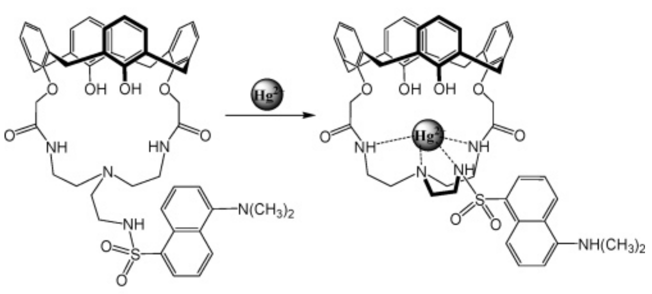

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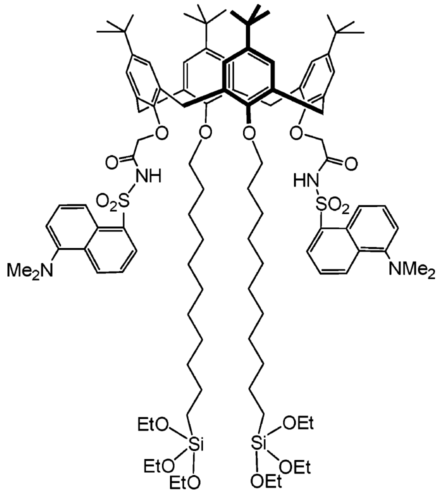
Chart 18



30

a strong quenching of the fluorescence, giving a detection limit of 3.3×10^{-7} mol/L, with a very high selectivity over interfering cations. In an acetonitrile−water mixture (60:40, v/v) at pH 4, Hg(II) complexation causes a slight blue shift (20 nm) of the emission due to deprotonation of the coordinated sulfocarboxamide group of the dansyl fluorophore. This work showed the utility of combining the complexing and photophysical properties of a well-tried fluoroionophore with a well-defined mesoporous silica to obtain a fully optimized system for mercury sensing. The use of a mesoporous silica as a support for grafting fluoroionophores opens up new opportunities for developing efficient sensors for heavy metals in water.

Apart from their application for metal ion sensing, calixarenes attached to a fluorophore can be used for pH sensing. The BODIPY-appended calixarene **31** (Chart 19) is such a sensor, acting through a PET mechanism.[120] The emission intensity of **31** in CH_3OH/H_2O (1:1, v/v) is strongly and reversibly pH dependent. There are more than 10-fold changes in the emission intensity, maximizing in the pH range 5.6−8.2. PET in this system can be explained by electron transfer from the electron pair located on the phenolate to the BODIPY moiety.

Chart 19

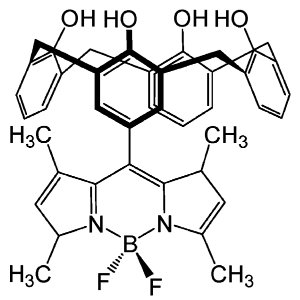


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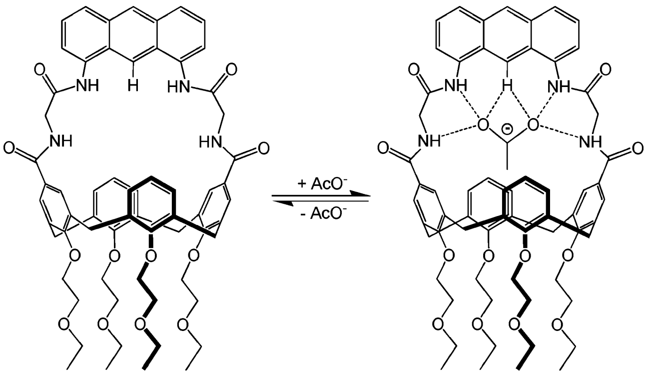
Chart 20



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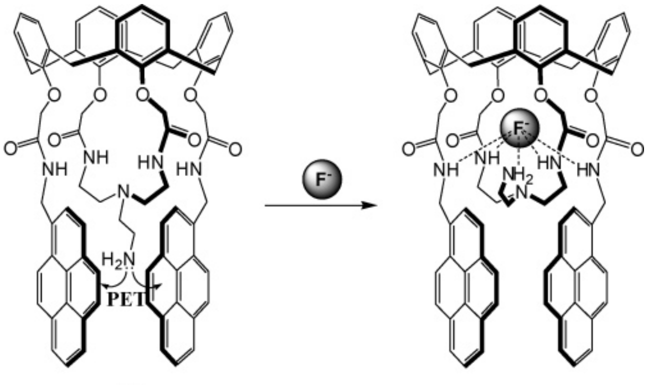
Fluorescent chemosensors for anions are less numerous than those for cations.[121a] Known fluorophore−anion interactions commonly involve bound hydrogen, especially amide NH. **32** (Chart 20) exhibits a selective interaction with CH_3COO^- in CH_3CN (0.4%, v/v, $CHCl_3$) over other anions tested.[121b] The addition of this anion to **32** leads to a quenching in fluorescence due to PET from nitrogen to the anthracene unit. ^1H NMR spectra indicate that oxygen atoms of the anion interact with the anthracene 9H as well as the amide NH centers.

Compounds **13** and **14** mentioned above are selective for F^-. However, unlike the complexation of Pb^{2+}, here both excimer and especially monomer emissions decrease.[94] The quenching in monomer emission is due to the PET effect from F^- to pyrene units, and that in excimer emission results from the hydrogen bonding between F^- and the amide groups linked to the fluorophores, which keeps the two pyrenes overlapping. **13** and **14** are selective for F^- in CH_3CN over other anions tested. This ion coordinates with **13** and **14** via hydrogen bonding with the amine NH of the triazacrown ring, causing both monomer and excimer emissions to be quenched due to PET from F^- to the pyrene group. The binding motif between F^- and the azacrown in **13**, **14**, and **22** is the same and is shown below. In addition to the complexation with bound hydrogen, F^- was also reported to coordinate to boron in **33**, causing fluorescence quenching. The distance between the two acidic boron centers in calixarene **33** is 3.429 Å, favorable for F^- binding in $CHCl_3$ over other anions (Chart 21).[122]

Chart 21



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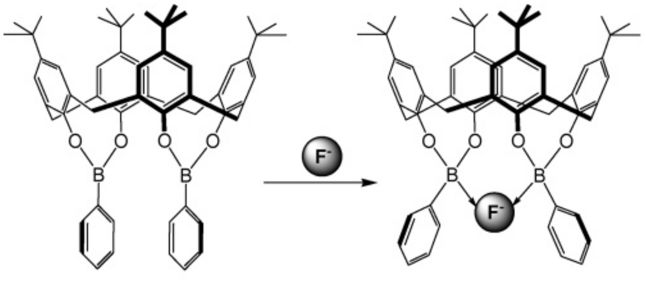

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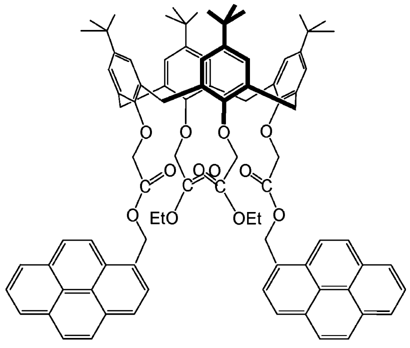
Chart 22



34

3.2. Excimer Sensors

As a fluorescent unit, pyrene is regarded as one of the most useful sensing molecules because it may emit as a monomer near 370−380 nm or as an excimer near 480 nm.[93,89] In molecules with two (or more) pyrenyl substituents, excimer formation can be efficient but is also sensitive to even subtle conformational changes such as may be induced by metal ion binding, so that the ratio (I_E:I_M) of excimer to monomer emission intensities can be an informative parameter in a variety of sensing systems.[7,93,123−126] For this reason, many pyrene-appended calixarenes have been synthesized and characterized.

Calix[4]arene derivative **34** (Chart 22), one of the first-reported calixarenes showing excimer formation, is a good chemosensor for Na^+ ion in MeOH/THF.[27] In **34**, *p-tert*-butylcalix[4]arene is used as the binding site because of its selectivity for Na^+.[127−131] The two pyrene units were introduced on the lower rim as fluorophores able to form an intramolecular excimer. The fluorescence spectrum of **34** shows a dual emission with the excimer at ca. 480 nm and the monomer at ca. 390 nm. In the absence of Na^+, the excimer emission is dominant compared with the monomer emission (I_E:I_M = 4:1). When **34** complexes with Na^+, the I_E:I_M ratio is altered by a change in the relative configuration of the two pyrene moieties induced by the reorientation of the four carbonyl groups of **34** to bind Na^+ ion. Examination of a Corey−Pauling−Koltun molecular model indicates an expanded distance between the two pyrene moieties caused by Na^+ binding. Addition of a 100-fold excess of another alkali-metal ion produces at most an 11% change in the ratio in the case of K^+ and a <1% change for Li^+, Rb^+, and Cs^+, showing that **34** may be useful to selectively sense Na^+ ion.

Compound **35** (Chart 23) with two fluorescent pyrene groups on the lower rim possesses a structure as well as properties similar to those observed in **34**.[28] When excited at 342 nm, it shows monomer and excimer emissions at ca. 380 and ca. 480 nm, respectively. Upon addition of metal ions to **35** in diethyl ether, the excimer emission sharply decreases. For uncomplexed **35**, NMR spectroscopy shows that there is an equilibrium between cone and partial-cone conformations, and the two pyrene units appear to be closer in the latter than in the former. Thus, the decrease in excimer emission upon the addition of metal ions may be explained as due to metal ion binding favoring the cone conformer.

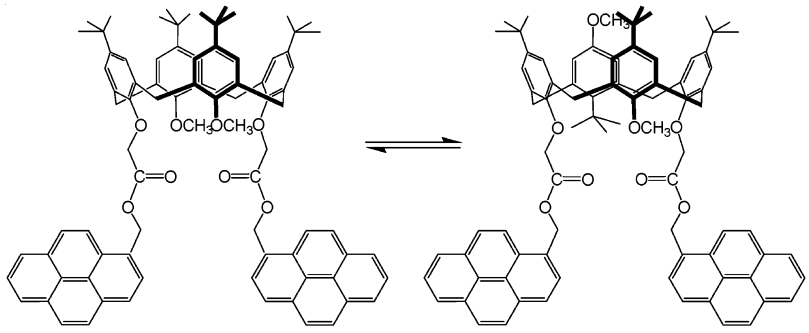
Matsumoto and Shinkai reported that the calixarene **36** (Chart 24), which bears an ionophoric cavity on the lower rim and two pyrene units on the upper rim, can be used for fluorescence sensing of some alkali-metal ions in CH_3CN/THF (1000:1, v/v).[132] The encapsulation of Li^+ or Na^+ into the ionophoric cavity induces a change in distance between the two pyrene moieties, which is reflected by a remarkable change in the I_E:I_M ratio. Addition of up to a 250-fold excess of K^+ does not affect the fluorescence spectrum of **36**·Li^+ or **36**·Na^+.

Calix[4]arene **37**, substituted at the lower rim by two 1,3-distal hydroxamate-based complexing arms, each incorporating a fluorescent pyrene receptor group, was reported to be selective for Cu^{2+} and Ni^{2+} in CH_3OH/H_2O (4:1, v/v).[133] The ligand alone shows monomer and excimer emissions which can be completely quenched by both Ni^{2+} and Cu^{2+} at different particular pH values which reflect the difference in the stability constant values for the two metals. Other transition metals are too weakly complexed for effects to be observed.

Reinhoudt et al. prepared the calixarene **38** with two substituents attached via amide links to distal rings.[134] Compound **38** (Chart 25) exhibits monomer emissions with maxima at 385 and 395 nm and an excimer emission with a broad band at 480 nm. The addition of Na^+ in methanol to a solid surface-immobilized monolayer of **38** causes the monomer emission to decrease and excimer emission to increase. This differs from observations with **34**, presumably because of conformational differences between the amide and ester units which allow closer contact of the pyrene units in **38**. This system provides one of the few examples of the use of a monolayer of a selective receptor for detection of metal ions by fluorescence, offering an alternative to physical immobilization in membranes, which affects the selectivity and limits the response rates caused by the partition of ions into the membranes.

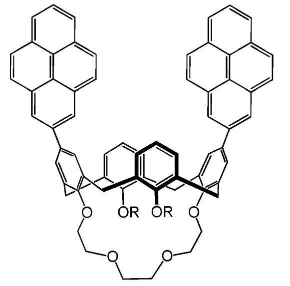
Kim et al. reported fluorescent calix[4]arenes **39** and **40** with two facing amide groups bridged to pyrene units.[135] These have distinctly different emission characteristics, **39** showing only monomer emission at 398 nm, while **40** shows a strong excimer emission, indicating that in the latter the

Chart 23

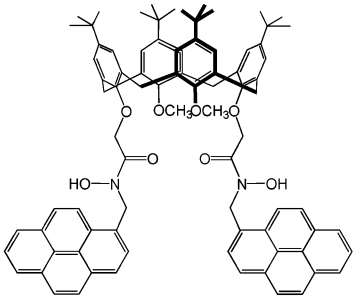


35

Chart 24

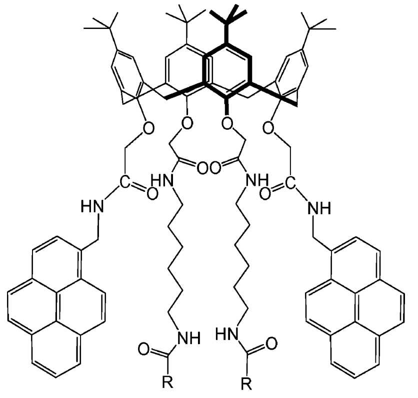


36



37

Chart 25

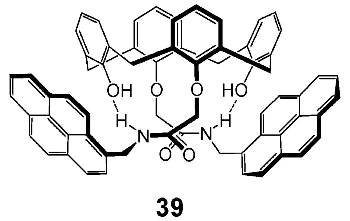


38

two pyrene units must be in close proximity, presumably as a result of $\pi-\pi$ stacking, while in the former they must be remote. These differences in orientation can be explained by the fact that intramolecular H-bonding is possible in **39** but not in **40**. For a calix[4]arene closely similar to **39**, an X-ray structure determination[135,136] has shown the residual phenolic groups to be involved in H-bonding, one to an amide NH unit, the other to an adjacent ether O, the result being that the pyrenyl substituents are divergently oriented and are thus too remote for excimer formation. It is assumed that this applies also in **39**, whereas for **40** the lack of H-bonding restrictions must allow the pyrenyl groups to adopt a face-to-face orientation.

Interestingly, **39** (Chart 26) exhibits a unique fluorescent response in the presence of In^{3+}, a cation known to interfere with iron metabolism at sites of absorption, transportation, utilization, and storage in cells. The addition of In^{3+} to **39** in CH_3CN enhances the excimer emission while the monomer emission is quenched. The phenomenon can be explained by In^{3+}-induced deprotonation of the phenolic OH groups, leading to the elimination of the hydrogen bonding between the phenolic OH groups and the amide groups. Conversely, upon the addition of In^{3+} to a solution of **40**, the excimer emission is quenched because the conformational change necessary for the initially divergent amide carbonyl oxygen atoms to bind to a single ion center is incompatible with retention of face-to-face π-stacking of the two pyrenes. The sensitive response of **39** to In^{3+} over other metal ions tested suggests that it can effectively serve as a fluorescent chemosensor for In^{3+}.

Chart 26



39

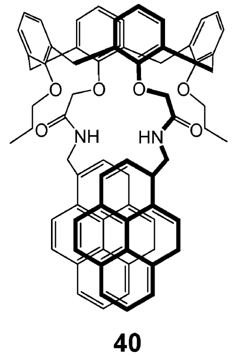


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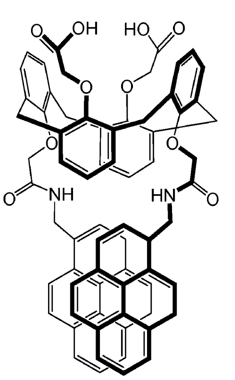
Chart 27



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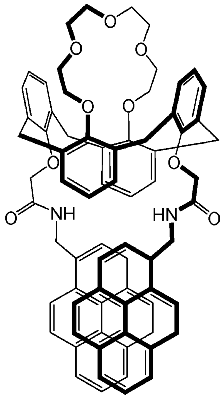
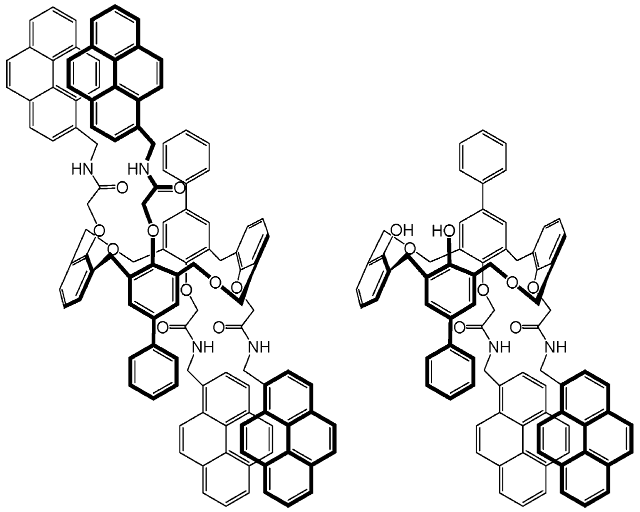


42

The calixarene dicarboxylate derivative **41**[137] (Chart 27) shows a significantly greater response to Ca^{2+} and Pb^{2+} than other cations tested, although while Pb^{2+} quenches both monomer and excimer emissions, with a major effect on the latter, Ca^{2+} enhances monomer emission and causes only a slight quenching, along with a blue shift of the emission peak, of the excimer band. This shift for Ca^{2+} may arise from less effective HOMO−LUMO interaction in the excited state. The excimer quenching produced by Pb^{2+} addition is in

Chart 28



43 **44**

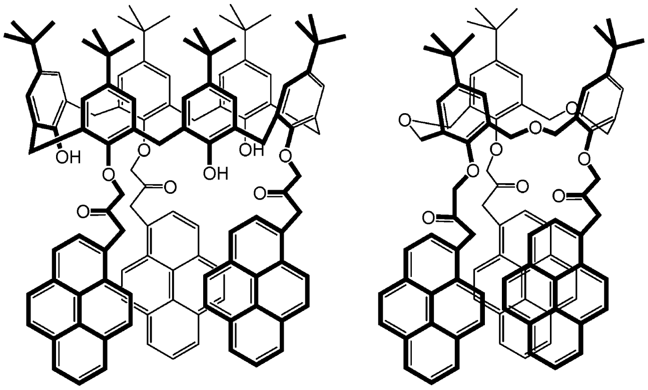
accord again with a conformational change associated with coordination of the amide carbonyl O atoms which increases the separation of the pyrenyl groups.[92,95] Interestingly, when Ca^{2+} is added to a solution of **41**·Pb^{2+}, both the monomer and excimer bands reappear. Comparison with the behavior of a similar calixarene lacking carboxylate groups indicates that Ca^{2+} must be sufficiently strongly bound at these sites to displace Pb^{2+} from its complex with **41**.

The 1,3-alternate calix[4]arene **42** with two bis(pyrenyl amide) groups and a crown-5 ring as substituents was reported to have properties similar to those of **41** in terms of changes in monomer and excimer emissions induced by metal ion addition.[92] The emission spectrum of **42** in CH_3CN shows a high sensitivity to Pb^{2+} and K^+ over other metal ions tested. The addition of Pb^{2+} considerably lowers the intensities of both the pyrene monomer and excimer emissions. The monomer quenching arises from reverse PET when Pb^{2+} ion is bound to the two carbonyl oxygen atoms, with the pyrene unit behaving as a PET donor to the carbonyl group. The excimer emission quenching is believed to occur as a result of conformational change caused by the two divergent amide carbonyl groups turning inward to bind Pb^{2+}. As with **41**, an on/off switch can be considered to operate in that **42**·K^+ provides an "on" state which can be converted to an "off" state by addition of Pb^{2+} and then returned to the "on" state by addition of K^+.

In a study of C-1,2-alternate tetrahomodioxacalix[4]arene pyrene amides,[138] it was observed that the fluorescence of **43** (Chart 28) in $CHCl_3/CH_3CN$ (1:3, v/v) shows a response to addition of Pb^{2+} similar to that of **41**, with both monomer and excimer emissions being quenched. Again, it appears that 1:1 coordination results in a conformational change which places at least two of the pyrene groups well apart. A more dramatic effect of Pb^{2+} binding is seen with **44**, where binding to the amide carbonyl oxygen donors in a 1:1 complex necessarily eliminates any possibility of excimer formation.

Unlike that of Pb^{2+}, the addition of Ca^{2+} to a solution of **44** induces an increase in excimer emission and a concomitant decrease in monomer emission. This can be explained by a different coordination mode for Ca^{2+} possibly involving chelation by the phenolic donors as well as the amide oxygen atoms, enabling the two pyrene units to become closer.

Chart 29



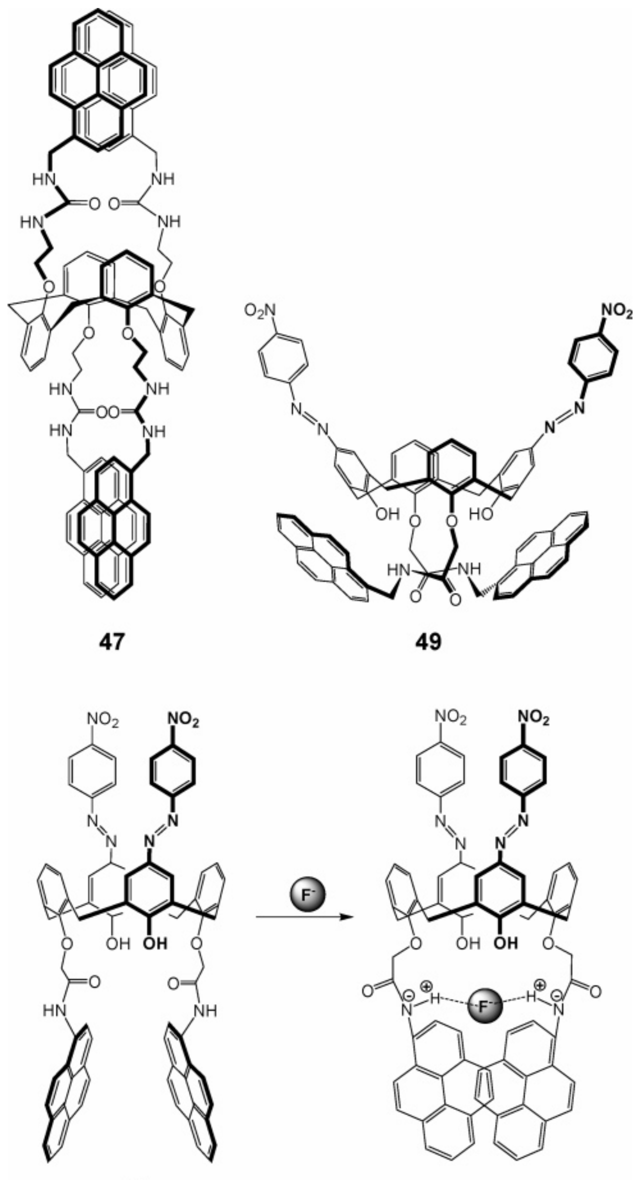
45 **46**

Various efforts have been made to develop sensors for nonmetallic cations. Takeshida and Shinkai reported that **45** (Chart 29) can be used to selectively recognize guanidinium ion (which is important in biological systems) in $CHCl_3$ in the presence of primary ammonium ions.[139] When excited at 346 nm, **45** shows monomer and excimer emissions at 396 and 487 nm, respectively. As the guanidinium ion concentration increases, the excimer emission intensity decreases while that of monomer emission increases, suggesting that guanidinium ion bound to the ionophoric $OCH_2C{=}O$ cavity prevents intramolecular contact of the pyrene moieties. These changes are almost unaffected by the presence of *tert*-butylammonium, protonated L-alanine methyl ester or *n*-hexylammonium ions. Compound **46** was also reported to be capable of binding guanidinium ion and inducing fluorescence changes, but the binding is competitively inhibited by primary ammonium ions.

As is apparent from the discussion above, most of the development of fluorescent calixarenes as sensors has concerned metal cations. This is unsurprising given the long-standing interest in calixarene coordination chemistry, but recently, however, interest has also begun to grow in the use of fluorescent calixarenes as anion sensors. This has again concerned pyrene-functionalized calixarenes, with H-bond donor groups as anion-recognition sites. For example, 1,3-alternate calix[4]arene **47** (Chart 30) with bis(pyrenylurea) groups on the lower rim, when excited, shows monomer and much broader (intramolecular) excimer emissions at 398 and 452 nm, respectively.[140] The I_E:I_M ratio remains unchanged at 4.4 in the concentration range from 10^{-7} to 10^{-5} M, as expected for intra- and not intermolecular excimer formation. Four urea groups providing eight possible H-bonds for anion binding are in close proximity to pyrene moieties, the relative orientation of which is thought to change upon anion complexation. Anion binding can thus be monitored by ratiometric changes in the emission spectrum (I_E:I_M ratio) of **47**. Of the anions tested, Cl^- causes the most marked changes in the emission spectrum of **47**. There is a strong quenching of the excimer emission with a corresponding enhancement in monomer emission. These observations suggest that the chloride anion may selectively coordinate with the urea protons in the cavity of **47** so as to "unstack" or lever apart the facing $\pi-\pi$-stacked pyrenes.

Kim et al. reported that calix[4]arenes **48** and **49**, which bear (4-nitrophenyl)azo and pyrene groups, are sensitive to F^- ion.[141] When excited at 343 nm, **48** exhibits a pyrene excimer emission at 480 nm.[135] Addition of F^- ion to **48** in CH_3CN produces a bimodal response in which initially the

Chart 30



47

49

48

Chart 31

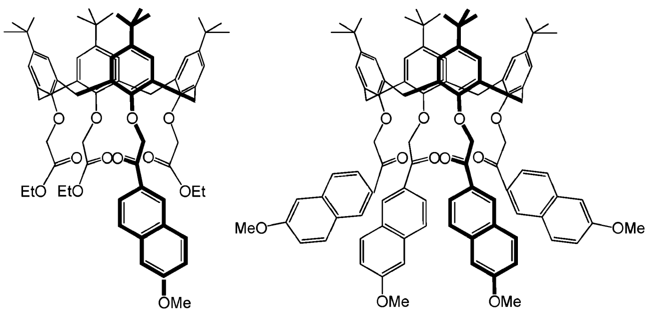


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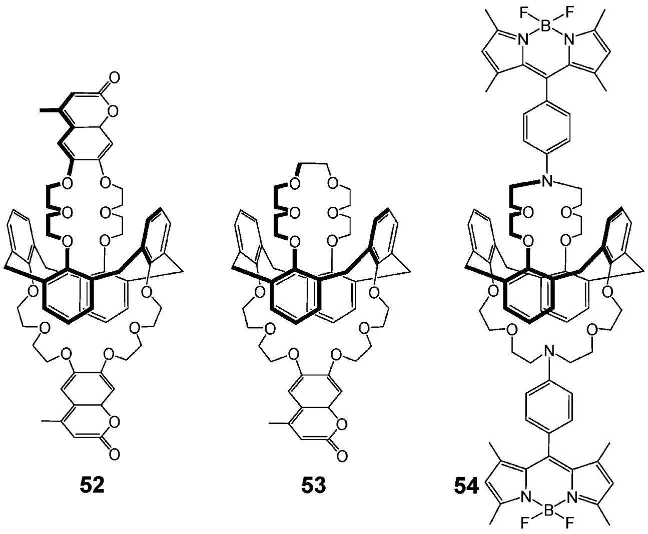
Chart 32



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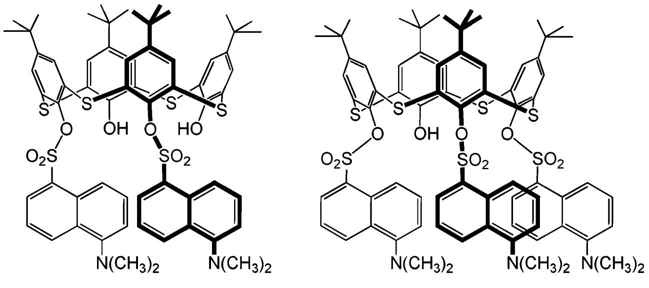
excimer emission is quenched but then a new species with emission bands at 385 and 460 nm appears. This behavior has been rationalized in terms of static pyrene dimer formation in the ground state influenced by H-bonding between F^- and the amide proton. The fluorescence of **49** also changes upon addition of F^- but in a different manner. In this case, the presence of a methylene spacer between the pyrene moiety and amide N probably forces the two pyrenes to be orthogonal to each other, as in a similar compound,[135] thus preventing the interaction which might give a dynamic excimer.[142]

3.3. PCT Sensors

Calixarene-based fluorescent sensors using a PCT mechanism have been widely exploited by Valeur et al. Compounds **50**[33,143] and **51**[143] bear, respectively, one and four 6-acyl-2-methoxynaphthalene fluorophores which contain the methoxy moiety as a donor unit and the carbonyl group as an acceptor in the PCT process (Chart 31). It was reported that the addition of metal ions to **50** and **51** in CH_3CN induces a red shift of the absorption and emission spectra associated with a major increase in fluorescence quantum yield due to the relative locations of the $n-\pi^*$ and $\pi-\pi^*$ levels depending on the charge density of the bound cation. In addition, for **51** interactions between the chromophores in the complexed molecule are reflected in a hypsochromic effect on the ground state as well as excimer emissions. Good Na^+:K^+ selectivity is seen in the stability constant ratios in a C_2H_5OH/H_2O mixture (8:2, v/v) of 500 for **50** and 407 for **51**.

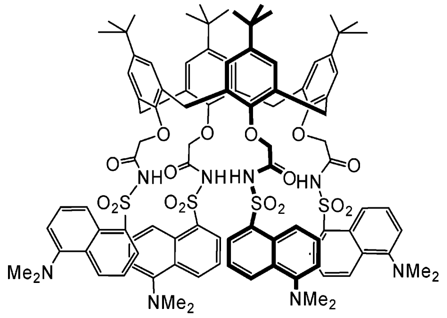
The incorporation of dioxycoumarin fluorophore(s) into one or both crowns of a calix[4]biscrown gives **52** and **53** (Chart 32).[144] For **52** in C_2H_5OH, the fluorescence emission band is blue-shifted and the fluorescence quantum yield is decreased upon addition of alkali-metal ions. This can be explained as due to the binding of the ions to the oxygen atoms at the 6- and 7-positions of the coumarin, causing a decrease in the electron-donating character of oxygen atoms and preventing the intramolecular charge transfer from the donor group at the 7-position to the lactone carbonyl moiety. The shorter the distance between the ion and oxygen atoms and the greater the charge density, the more efficient the quenching. Both 1:1 and 2:1 (metal:ligand) complexes form, in which the latter shows a larger cation-induced blue shift than that of the former, suggesting a stronger interaction between the cation and excited coumarin fluorophore in the 2:1 complex than in the 1:1 complex. This may be due to the electrostatic repulsion between the two cations, which makes them approach closer to the coumarin moiety in the 2:1 than in the 1:1 complex. The fluorescent behavior of **53** upon complexation of alkali-metal ions is similar to that of **52**. The selectivities for Cs^+ vs Na^+ and K^+ vs Na^+ of **52**,

Chart 33



55 **56**

Chart 34



57

expressed as the ratio of the stability constants of the 1:1 complexes, are 1.6 × 10^4 and 220, respectively, whereas, those of **53** are 4.0 × 10^4 and 540, respectively. Compounds **52** and **53** are not soluble in water, but they can be applied to determine cations in this medium by immobilizing them in a polymer or a sol−gel film.

Recently, Valeur et al. also reported the synthesis and fluorescent properties of **54**, a 1,3-alternate calix[4]azacrown-5 bearing a boron dipyrromethene (BODIPY) unit as a fluorophore.[145] The BODIPY unit can be excited at relatively long wavelengths (∼475 nm), an advantage in biological analyses because autofluorescence is thereby minimized. The BODIPY moiety in **54** shows a PCT effect in polar solvents, producing a dual emission and a quenching in fluorescence. Cation binding to the amino group blocks the PCT process, inducing a strong enhancement in fluorescence. Due to its high K^+:Na^+ selectivity in C_2H_5OH, **54** can be regarded as a potential K^+ sensor.

Thiacalixarenes **55** and **56** (Chart 33), containing the dansyl fluorophore, well-known for its sensitivity to the polarity of the medium due to intramolecular PCT, exhibit a fluorescent enhancement upon complexation of Cd^{2+} and some other transition-metal ions.[146a] Being soluble in water, both can be used to sense metal ions directly in aqueous solution by fluorescence changes. With only two dansyl moieties, **55** is less sterically congested than **56** and is thus a stronger host and a better sensor. Both also show the ability to sense some neutral molecules such as borneol, nerol, menthol, cyclohexanol, cyclooctanol, and 1-adamantanecarboxylic acid, the greatest sensitivity of both being to nerol because of its close fit to their cavities.

For compound **57**,[146b] the optimum pH for observation of the effects of Pb^{2+} binding is 5.2, at which point **57** is mainly in its neutral form (Chart 34). There, addition of Pb^{2+} causes a 52 nm blue shift of the fluorescence peak and a 1.7-fold enhancement of the fluorescence quantum yield. The absorption spectra are also shifted to higher energy (11 nm) upon Pb^{2+} binding. The blue shift is rationalized by the deprotonation of the sulfonamide group upon cation binding.

Calixarene-based fluorescent sensors showing PCT were also reported by Kim et al.[147a] Compound **58** (Chart 35) containing two cation recognition sites, a crown ether ring and two facing pyrene amide moieties, shows a drastic change in the fluorescence and absorption spectra in CH_3CN upon complexation of Pb^{2+}, Cu^{2+}, or K^+ with different

Chart 35

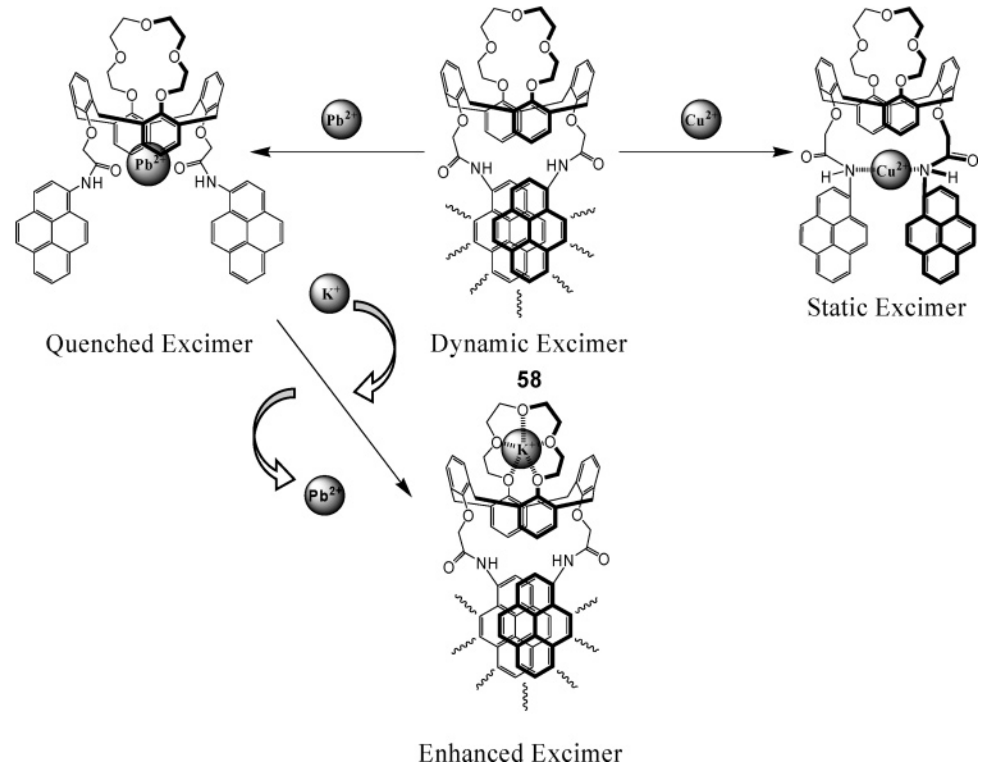


Chart 36

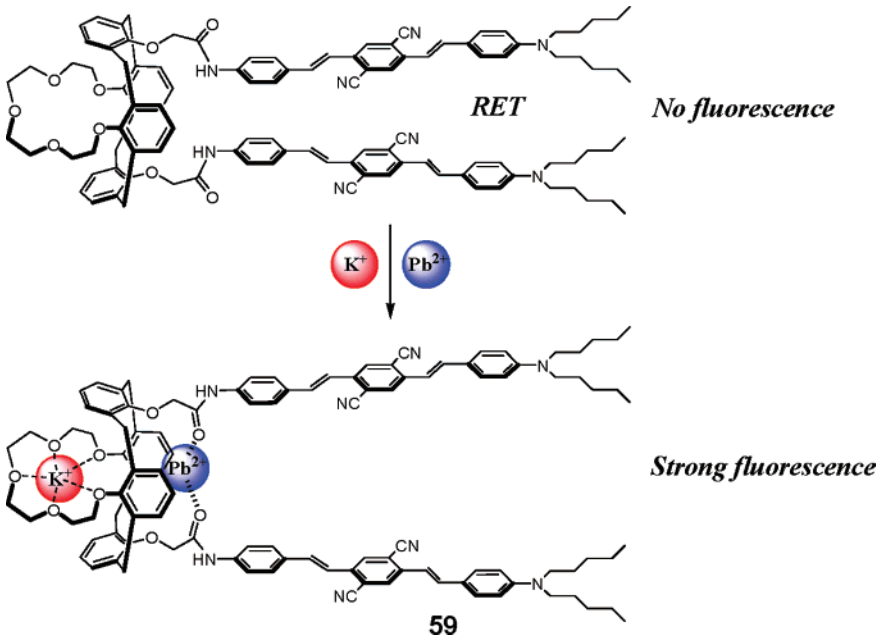
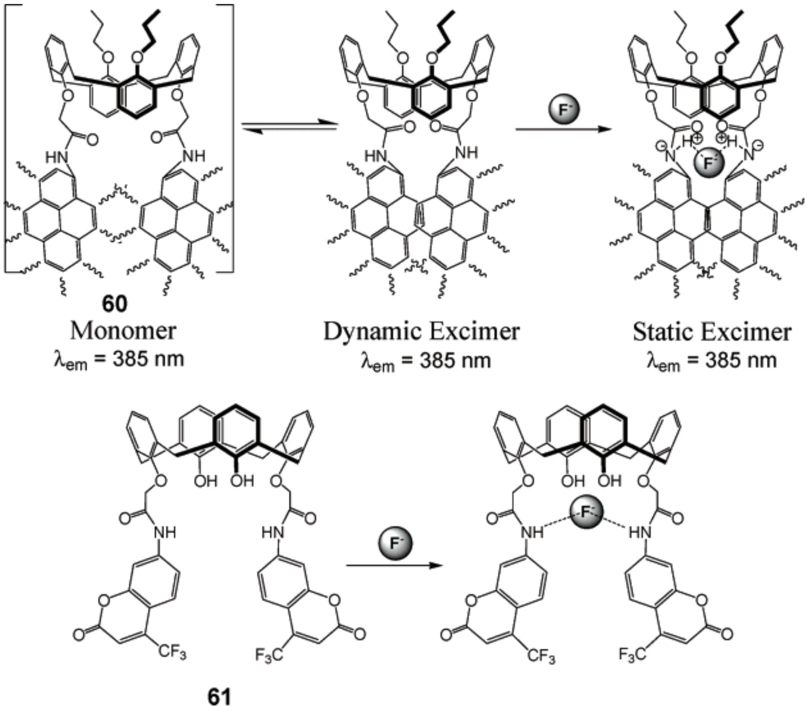


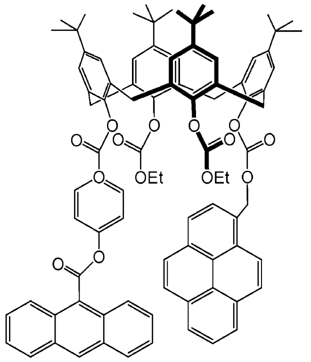
Chart 37



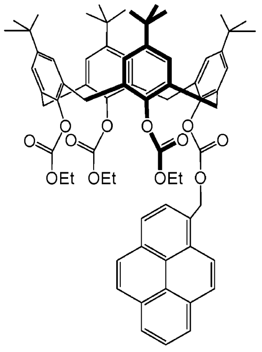
binding modes.[147a] N···Cu^{2+}···N chelation makes the distance between the two pyrenes shorter, resulting in a static excimer evidenced by a red shift in the excitation spectrum of its complex. Conversely, C═O···Pb^{2+}···O═C coordination forces the two pyrenes apart, allowing no static excimer formation at all. Complexation of both Cu^{2+} and Pb^{2+} reduces the emission intensity. The addition of K^+, however, makes the excimer emission increase, presumably because the polyether ring of calix[4]crown-5 is more suitable for complexation of K^+. Only Cu^{2+} induces shifts in both the fluorescence and absorption maxima, and these are attributed to a PCT process.

Compound **59**[147b] (Chart 36) bearing chromophores capable of two-photon absorption has been synthesized by Kim et al. Its responses to metal ion binding were investigated via absorption band shifts as well as one- and two-photon fluorescence changes. The free ligand absorbs at 461 nm and emits weakly at 520 nm, the weakness of this emission being attributed to self-quenching due to resonance energy transfer (RET) between the two adjacent chromophores. Fluorescence due to two-photon absorption at 780 nm is indetectable but is considerably enhanced, as is that from single-photon excitation, when various metal ions are bound. Addition of Al^{3+} or Pb^{2+} ions to a solution of the ligand causes a blue shift in absorption (385 nm) and enhanced fluorescence at 520 nm due to a weakened RET consequent upon the conformational change due to coordination causing the chromophores to be more divergently oriented. Interestingly, binding of K^+ in the crown ring appears to produce an allosteric effect favoring Pb^{2+} binding, as addition of the

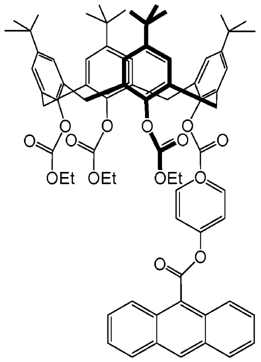
Chart 38



62

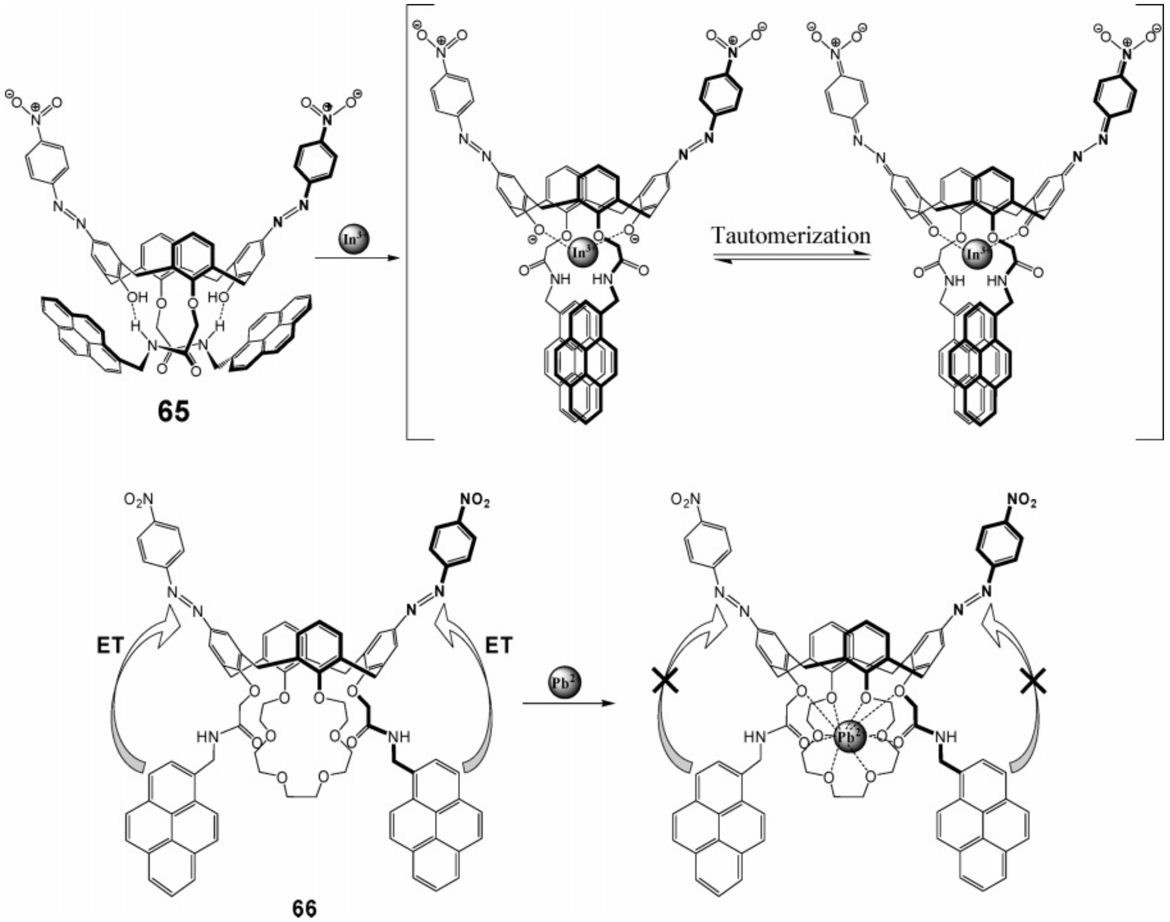


63



64

Chart 39



Pb^{2+} to a solution of **59**·K$^+$ results in a higher fluorescence intensity than in the simple **59**·Pb^{2+} complex.

Again, anion sensing based on PCT has as yet been developed much less than that of cations, but recently, Kim et al. reported that **60**[142] with two fluorescent pyrenes and **61**[148] with two coumarins can be used to selectively sense F$^-$ ion (Chart 37). When excited at 346 nm, **60** shows monomer and excimer emissions at 385 and 482 nm, respectively. The addition of F$^-$ to **60** in CH$_3$CN induces a 54 nm red shift of the absorption band and a 12 nm blue shift of the excimer emission band with an enhancement of the fluorescence intensity, the latter shift being due to formation of a static excimer in the ground state. When **61** is excited at 335 nm, it exhibits an emission band at 420 nm, which is quenched upon complexation of F$^-$ in CH$_3$CN to give rise to a weak band at 508 nm. The addition of F$^-$ to **61** causes a decrease in emission intensity together with a red shift, which results from H-bonding followed by protonation.

3.4. FRET Sensors

Compared with calixarene-based fluorescent sensors using PET, excimer, or PCT mechanisms, those using FRET have been rarely reported. Compound **62**, containing anthroyloxy as an acceptor and pyrene as a donor, is one example (Chart 38).[149] The overlap between the emission of **63** (containing the donor) and the absorption of **64** (containing the acceptor) suggests that there should be an intramolecular fluorescence energy transfer from pyrene to anthroyloxy in **62**. The experiment shows an increase in emission intensity of the anthroyloxy group of **62** compared with that of **64** (ca. 2.5-fold) and a decrease in emission intensity of the pyrene monomer of **62** compared with that of **63** (ca. 10-fold), indicating that the energy transfer takes place in **62**. The complexation of Na^+ or K^+ in CH_3OH/THF (15:1, v/v) induces major changes in the emission intensity, with the effects being greater for Na^+ than K^+.

Recently, Kim et al. reported that **65**[135] and **66** (Chart 39),[150] bearing pyrene as a donor and (*p*-nitrophenyl)azo as an acceptor, show FRET effects. It is believed that the electron transfer from the pyrene units to the nitro groups is partially involved in weakening the emission of **65**. The complexation of In^{3+} in CH_3CN causes a dramatic red shift from 380 to 507 nm, which supports In^{3+} binding to the phenolate oxygens formed by deprotonation of the phenolic OH groups to facilitate the quinone−hydrazone tautomerization. In **66**, the notable fluorescence quenching is obviously due to a significant spectral overlap between the fluorescence emission band of pyrene units as a donor and the absorption band of azophenyl units as an acceptor. The complexation of Pb^{2+} in CH_3CN induces an increase in the pyrene emission that can be explained by diminished overlap of the donor and acceptor bands caused by a hypsochromic shift of the azo unit absorption by complexation, resulting in a diminished FRET effect. Compound **66** can be used as a FRET-based selective fluorescent sensor for Pb^{2+}.

4. Conclusions

This review deals with calixarenes used as fluorescent reagents for sensing anions and cations, with a focus on the major mechanisms which control luminescence behavior. While many prospects for the utilization of calixarenes in cation and anion analysis have been demonstrated, these have largely concerned analyses in organic solvents, and the results are less encouraging for aqueous systems. Nonetheless, promising results have been obtained for calixarenes immobilized on a matrix suitable for use with aqueous media and with calixarenes functionalized so as to make them water-soluble. However, such studies are rare, and the development of new highly selective sensing systems applied in aqueous media is still one of the major challenges for the chemist.

The unique topology of calixarenes offers a wide range of scaffolds, enabling them to encapsulate many different ions. Some have been studied for the determination of toxic cations such as In^{3+}, Pb^{2+}, Cu^{2+}, Ag^+, and Hg^{2+} ions. Significantly, they can be used for the determination of alkali-metal ions, for which the design of effective complexing agents is generally difficult. It should be noted that there are relatively few examples of anion sensing in comparison with those for cations but there are reports of fluoride ion sensing, and the design of calixarene-based fluorescent sensors for biologically and environmentally relevant anions such as cyanide, lactate, nitrite, nitrate, and borate is an attractive prospect.

Bonds formed between a metal complex and an anion are stronger than those formed by hydrogen-bonding or electrostatic interactions, but no report related to anion sensing based on its interaction with a metal complex has been shown, and a study on this line should be taken into consideration for calixarenes. The analysis of sensor properties in this review offers some understanding at the fundamental level of the chemical and photophysical factors involved and illustrates the prospects for a number of analytical applications in environmental and biological areas.

5. Acknowledgments

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