SENSING MECHANISMS - CHEMOSENSORS

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Abstract: The present research article elaborates different sensing mechanisms of chemosensors based on photophysical processes, such as, photoinduced electron transfer (PET), charge transfer (CT) etc. A brief introduction about types of chemosensors is followed by detailed discussion of various mechanisms.

IndexTerms- Chemosensor, mechanisms, colorimetric, fluorescent.

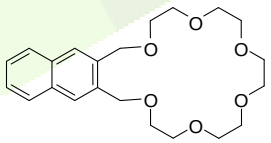
1. Introduction

Development of optical chemosensors is ever growing area of research for last four decades. The concept of various optical sensors originated from molecular recognition which employed different approaches. All these approaches involve the presence of a signaling moiety (indicator) which can be a chromophore or a fluorophore resulting in chromogenic or fluorogenic sensors, respectively.

Colorimetric/chromogenic sensors are especially attractive because the guest determination can be carried out by the naked eye, without the use of expensive equipment and they also find direct applications in the development of optodes and disposable dip-stick arrays based on absorption changes. In colorimetric sensors, a bathochromic or hypsochromic shift of absorption band or visual color change is affected by the respective increase or decrease in electron densities on the chromophore moiety which is more effectively carried by the association of a charged analyte i.e. cation or anion than a neutral molecule. The interaction of guest / analyte species with the receptor occurs only in its ground state.

In the case of fluorescent chemosensors, the observed change in the fluorescence emission could be due to interaction of the analyte with the chemosensor in the ground state which results in formation of new chemical ensemble with different emission properties. Alternately, the analyte may preferentially interact with the excited state of the chemosensor resulting in either change in life time of the excited state resulting in change in the emission intensity or leading to new excited state with different emission properties. The excitation of the chemosensor also results in change in the electron distribution within the chemosensor and thus may enhance / lower the interaction of the chemosensor with the analyte. Thus, the possibility of variation in the excited state of the chemosensor both due to (i) interaction of the guest / analyte with the chemosensor in the ground state or in the excited state (PET) (ii) reorganization of the excited state (ESIPT, TICT, FRET etc.) provide significantly more possibilities for interaction of an analyte with the chemosensor in excited state than that observed in the ground state.

In a normal fluorescence process, an electron is excited from the HOMO to the LUMO of the molecule to achieve singlet excited state. The vibrational relaxation of the excited state prior to emission of a photon from the excited state leads to decrease in energy of the emitted radiation. This decreased energy of the emitted radiation from the absorbed radiation is manifested as red shift of the emission spectrum – termed as "Stokes shift".



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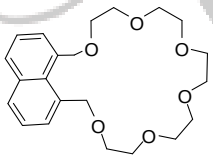

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Sousa reported that naphthalene compounds **1** and **2** were perturbed by various alkali metal chloride salts causing increase and decrease in fluorescent quantum yield, phosphorescence quantum yield, and phosphorescence lifetime.[1] This is the first study of perturbation of excited state using a non-covalently held species.

Several research groups have employed the fluorophore-spacer-receptor[2] design for fluorescent chemosensor including Czarnik[3], Fabbrizzi[4], Tsien[5], Shinkai[6], de Silva and many others.[2] Based on different photophysical processes, different sensing mechanisms viz. photoinduced electron transfer (PET), charge transfer (CT), energy transfer (ET), excimer / exciplex formation have been elaborated.

2. Sensing Mechanisms

2.1 Photoinduced Electron transfer (PET)

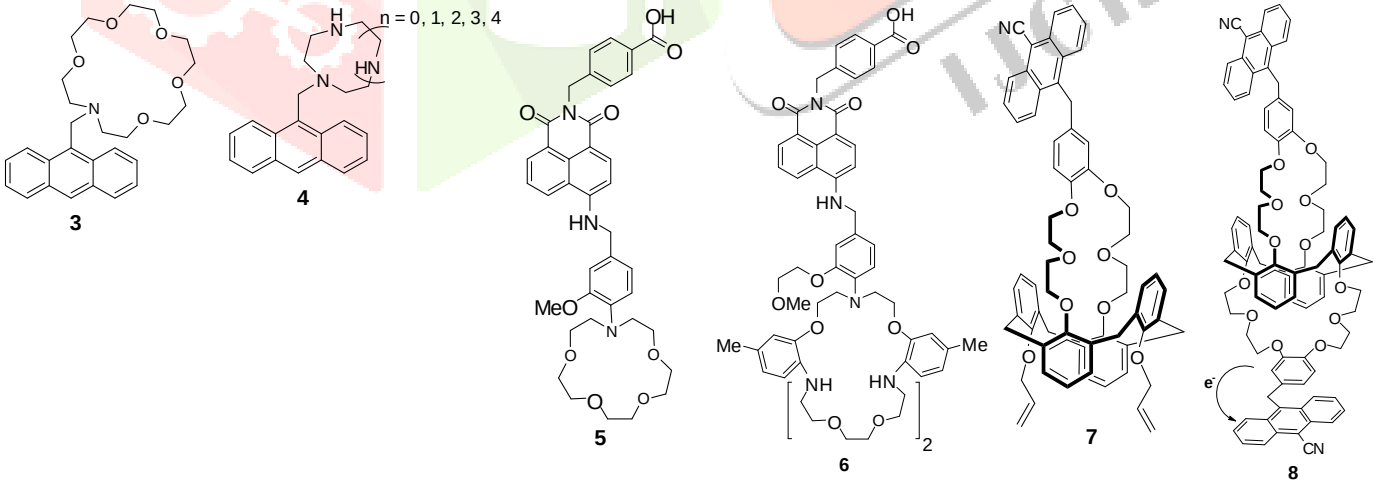
Electron transfer (ET) is one of the most important chemical process in nature and it plays a central role in many biological, physical and chemical (both organic and inorganic) systems. In nature, ET occurs in photosynthetic reaction center where transfer of electrons is used to create charge imbalance across a membrane, originating a proton pumping mechanism to produce ATP. In chemical systems, ET at the metal surface with oxygen is responsible for the corrosion. Solid state electronics depends on the

control of the ET in semiconductors and the new area of molecular electronics depends critically on the understanding and the control of the transfer of electrons in and between molecules. Electron transfer can occur thermally, electrically and photochemically. The latter process is referred to as photoinduced electron transfer (PET) that has been most widely employed in the fluorescent chemosensors. In the simplest case of fluorescence, the emission of a photon follows HOMO to LUMO excitation of an electron in a molecule. Where this emission is

Figure 1 (a) Representation of PET in the fluorophore-spacer-receptor approach when bound and unbound. (b) Frontier orbital diagram of the PET in the fluorophore-spacer receptor approach. (c) CHEF

efficient, the molecule may be termed a fluorophore. When a lone electron pair is located in an orbital of the fluorophore itself or an adjacent molecule and the energy of this orbital lies between those of the HOMO and LUMO, the 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 photoinduced electron transfer provides a mechanism for non-radiative deactivation of the excited state (Fig. 1), leading to a decrease in emission intensity or "quenching" of the fluorescence. The protonation or binding of a metal ion with lone pair 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).

N-Anthracenylmethyl-aza-18-crown-6 **3**[7] shows a weak fluorescence (Φ = 0.003). On binding with K^+ in methanol, the quantum yield of fluorescence was enhanced to Φ = 0.14. So, the coordination of lone pair with K^+ inhibited PET and released fluorescence. Similarly, polyazamacrocycle **4**[8] on binding with Zn^{2+} exhibited 25-fold enhanced quantum yield.



The blood electrolyte levels in serum and whole blood samples are measured quickly and reliably with a family of fluorescent PET sensors **5** and **6**. The fluorescence intensity of PET sensor disk **5**[9] (pH 7.4, 100 mM HEPES buffer) at 560 nm (λ_{ex} = 470 nm) increases substantially with increasing concentrations of sodium. Binding of the cation to the azacrown ether inhibits fluorescence quenching by the anisidine donor. The fluorophore does not directly interact with the sodium cation. As a result, the excitation and emission maxima are nearly invariant with changing sodium concentrations.In comparison with 140 mM of sodium, the physiological concentrations of other cations, such as potassium (4.5 mM), calcium (1.2 mM), and magnesium (0.5 mM), in blood or serum are very low. Therefore, the interferences from these ions were negligible. Similarly, sensor disk **6**[10]selectively binds with K^+ ion and is used for practical measurement of extracellular (serum or whole blood) potassium.The green fluorescence intensity (pH 7.4 TRIS-HEPES buffer) at 540 nm increased substantially with increasing concentrations of K^+. In the clinically

important concentration range between 2 and 10 mM potassium, a 5.8% signal change permillimolar of potassium was observed. Time required for the binding was less than 1 minute.

Chemosensors **7** and **8**[11,12] showed weak emission at ~ 430 and ~ 450 nm due to the PET from the oxygen atoms of the benzo moiety to the excited singlet state of the cyanoanthracene fluorophore. The emission intensities of **7** and **8** in CH_2Cl_2-CH_3OH wereenhanced by a factor of 8.2 and 11.7 fold, respectively on addition of Cs^+. These fluorescence enhancements could be attributed to inhibition of PET due to coordination of oxygen atoms with Cs^+.

2.2 Charge transfer (CT)

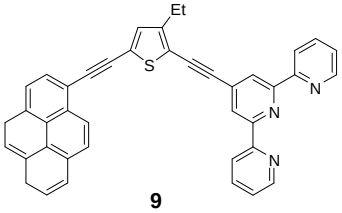
Electronic excitation necessarily involves some degree of charge transfer, but in fluorophores containing both electron-withdrawing and electron-donating substituents, this charge transfer may occur over long distance and be associated with major dipole moment change, making the process particularly 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. For example, on complexation of cation with an electron-donor group within a fluorophore, the electron-donating 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 electron-acceptor group enhances its electron-withdrawing character, and the absorption spectrum is red-shifted with an increase in molar absorptivity (see Fig. 2). The fluorescence spectrum should be shifted in the same direction as the absorption spectrum, and in addition to these shifts, change in the quantum yield and lifetime can also be observed. All these photophysical effects are obviously dependent on the charge and the size of the cation, and therefore, some selectivity is expected.

Figure 2 CT system

Charge transfer processes include intramolecular charge transfer (ICT), metal–ligand charge transfer (MLCT), and twisted intramolecular charge transfer (TICT). For an ICT-based chemosensor, enhancement or suppression of such an ICT process can lead to a red or blue shift in its emission spectrum, thus resulting in a ratiometric signal which can eliminate most ambiguities by self-calibration of two emission bands, and allow quantitative determination in more complex applications, such as imaging in living cells and tissues. In case of MLCT, charge transfer from a ligand to the transition metal cation, is commonly observed in transition metal complexes, such as those of ruthenium, rhenium and iridium, etc. It is also used for design of chemosensors through the influence of MLCT energy level by analytes. In addition, TICT is a strong intramolecular charge transfer process occurring in the excited state that involves solvent relaxation around the molecule to yield a continuing rotation of electron-donor and acceptor until it is twisted about 90°.[13,14] Since the polar solvent relaxation is necessary for the intramolecular rotation and charge separation in the TICT state, the fluorescence behavior is very sensitive to micropolarity and/or steric hindrance for molecular rotation[15].

2.2.1 Intramolecular charge transfer (ICT)

Chemosensor **9**[16]is an ICT sensor with a terpyridine (tpy) receptor and a π-electron system spreading over a pyrene moiety through 2,5-diethynylated thiophene connector. On addition of Zn^{2+} to the solution of **9** in CH_3CN, both the absorption and fluorescence bandsat 426 and 480 nm were red shifted to a broad band in 400-500 nm region and a new emission band at 600 nm, respectively. The water soluble phenoxazinone based chemosensor **10**[17]exhibited blue-shift of the absorption bandfrom 585 nm to 469 nm associated with color change from pink to yellow, on addition of Hg^{2+}. The emission spectrum also showed a small blue-shift from 634 nm to 615 nm, besides a degree of quenching. This allowed ratiometry inabsorption, as well as emission channels. The lowest detection limit for Hg^{2+} was 100 nM. Calix[4]arene based chemosensor **11**[18] showed blue shift of 52 nm in the fluorescence spectrum from 565 nm to 515 nm on addition of Pb^{2+}.



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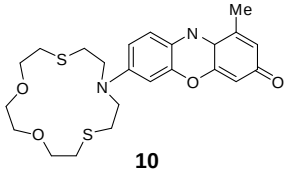

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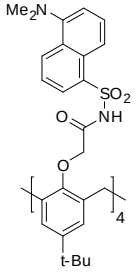

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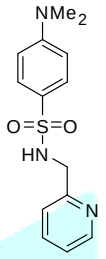
2.2.2Twisted intramolecular charge transfer (TICT)

In the TICT mechanism, rotation around a bond connecting a donor group and an acceptor group can decouple the orbitals of these two groups. This orbital decoupling provides a means by which nearly complete electron transfer from the donor to the acceptor can occur. A highly polar twisted excited state under appropriate solvent conditions, can be preferentially stabilized with respect to a planar local excited state. Since the highly twisted form is energetically destabilized in the ground state, TICT formation brings the excited and ground states closer, permitting more rapid internal conversion.

Chemosensors **12**[19] and **13**[19] showed dual fluorescence, originating from a locally excited (LE) state and a TICT state, respectively at 360 nm and 475 nm. These two states are less resolved in case of **12**. In acetonitrile-borate buffer (1:1), the fluorescence intensity of **12** was quenched on addition of Cu^{2+} due to the usual PET and sulfonamide deprotonation. In the case of **13**, only the TICT band was quenched on addition of Cu^{2+} whereas addition of Zn^{2+} (d^{10}) greatly enhanced the LE band by 17 times.

Compound **14**[20]is an extreme case of TICT.Compound **14** showed a 37-fold fluorescence enhancement on addition of Ca^{2+} in acetonitrile. Ca^{2+} binds to the podand and both carbonyl oxygen atoms to prevent the twisting necessary for the population of a TICT state. Sr^{2+} was less effective, whereas Ba^{2+} and Mg^{2+} showed no change in fluorescence.



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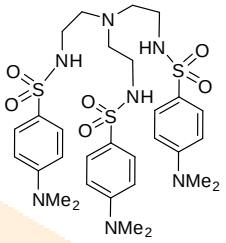

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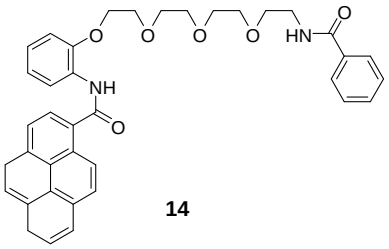

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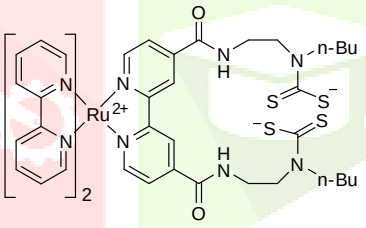
2.2.3Metal to ligand charge transfer (MLCT)

In a very simple approach, a complex in a MLCT state can be viewed as an isomer of the ground state which contains an oxidized metal and reduced ligand. The excited state reactivity can then be ascribed to the nature of the oxidized metal center or/and reduced ligand.

Chemosensor **15**[21] exhibited λ_{em} at 597 nm due to MLCT which on addition of $H_2PO_4^{2-}$ in its CH_3CN solution was quenched by more than 88%. The bipyridyl-Re(I) tricarbonyl lumophore coupled to an amide hydrogen bonding site in chemosensor **16**[22] exhibited triplet MLCT luminescence at 524 nm which was quenched on addition of CN^- or halides in CH_2Cl_2.



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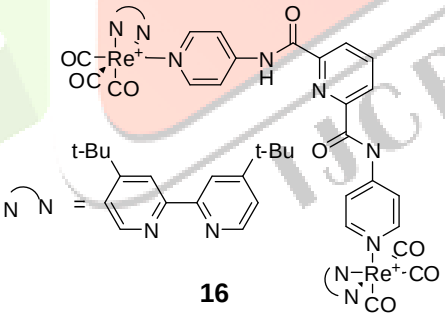

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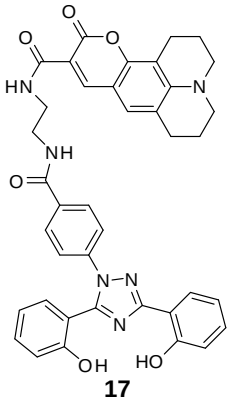
2.3 Energy transfer

The fact that energy runs downhill and excited state of high energy can donate energy to another molecule to populate its excited state with relatively lower energy. Since each excited state can emit its own signature, it provides the conditions for a two-color sensory system. The intensities of the two wavelengths can be rationed. The efficiency of donation / transfer of energy is crucially dependent on the distance between the two concerned states. There are two possible mechanisms for energy transfer: (i) electronic energy transfer (EET) and (ii) fluorescence resonance energy transfer (FRET) based on the distance between the energies of a donor and the acceptor.

2.3.1 Electronic energy transfer (EET)

In EET, two electrons are exchanged in a correlated manner between the donor and acceptor, one between the HOMOs, and one between the LUMOs of these molecules. EET is also called Dexter electron transfer, is efficient if a distance between the donor and the acceptor is within 10 Å. At smaller distances, orbital overlap between the two states dominates. This Dexter mechanism, is particularly important in the case of energy transfer between triplet states, because the direct process is then forbidden.



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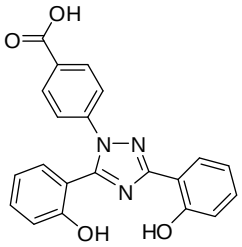

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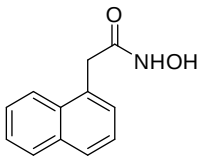

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Chemosensors[23]**17** and **18**, in the Al^{3+}-free state have a very small excited state lifetime owing to the vibrational coupling of the phenolic unit with water. Hence, EET process is very inefficient and **17** gives very little emission from the aminocoumarin. The emission of **18**.Al^{3+}, however, overlaps well with the absorbance of the aminocoumarin unit. Direct excitation of the aminocoumarin shows no Al^{3+}-induced FE, confirming that the aminocoumarin is not involved in the binding process. On the other hand, the Al^{3+}-bound state of **17** has a much longer lifetime for the excited state of phenolic unit, which allows excellent EET to the aminocoumarin and fluorescence emission due to aminocoumarin.

Chemosensor**19**[24] undergoes switch 'off' of its structured band with λ_{em} at 325 and 340 nm (naphthalene- like fluorescence) upon binding with Fe^{3+} in 50% aqueous methanol. There is also an appearance of a charge transfer absorption band at longer wavelength. The latter is the probable sink for the EET process, though a contribution from PET to this redox-active ion is also probable.

2.3.2 Forster resonance energy transfer (FRET)

Förster resonance energy transfer (FRET) refers to the non-radiative transfer of an electronicexcitation from a donor molecule to an acceptor molecule[25,26].

$$D^* + A \rightarrow D + A^*$$

This electronic excitation transfer, whose practical description was first given by Förster, arises from a dipole-dipole interactionbetween the electronic states of the donor and the acceptor, and does not involve the emission and re-absorption of the light. Transfer occurs when the oscillations of an optically induced electronic coherence on the donor are resonant with the electronicenergy gap

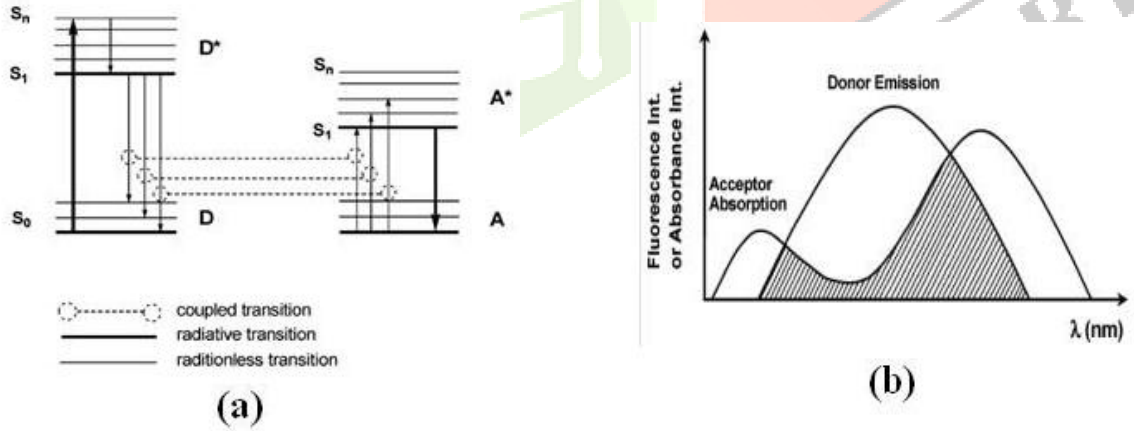
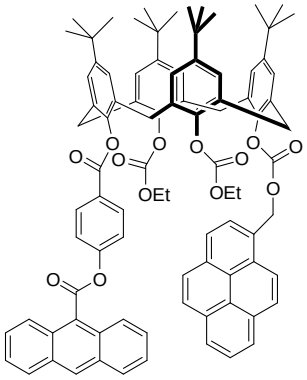


Figure 3 (a) Fluorescence (Forster) Resonance Energy Transfer System **(b)** Spectral overlap for FRET (reproduced from Chem. Rev. 2007,107, 3780-3799).

of the acceptor. So, Förster transfer is a dipole-dipole coupling mechanism. This process involves Coulomb (electrostatic) interactions between the charge distributions in the two molecules, so that the excited molecule (the donor) goes from its excited to its ground state, while the other one (the acceptor) inversely goes from its ground state to its own (energetically lower) excited state. This process can be seen as the exchange of a virtual photon, as the electrons remain localized on their respective molecules. The strength of the interaction depends on the magnitude of a transition dipole interaction, which depends on the magnitude of the donor and acceptor transition matrix elements, and the alignment and separation of the dipoles. The distance between the donor and acceptor should be from 10 to 100 Å for efficient FRET to occur. Thus, the efficiency of energy transfer process is very much distance dependent. It requires a certain degree of spectral overlap between the emission spectrum of the donor and the absorption spectrum of the acceptor (Fig. 3).

Compound **20**[27] shows ~ 2.5- fold increase in emission intensity of the anthroyloxy group of **20** compared with that of **22** and a 10-fold decrease in emission intensity of the pyrene monomer of **20** compared with that of **21** which is assigned to FRET from pyrene to anthroyloxy group. The complexation of Na^+ or K^+ in CH_3OH-THF (15:1) induces significant change in the emission intensity, as the emission intensity of the anthroyloxy group at 480 nm increased significantly compared with that of the pyrene monomer (~385 nm), with the effects being greater for Na^+ than K^+.



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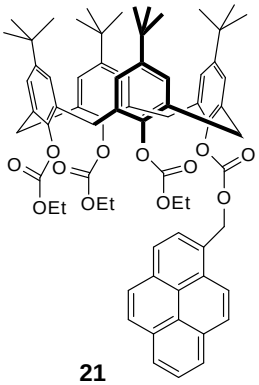

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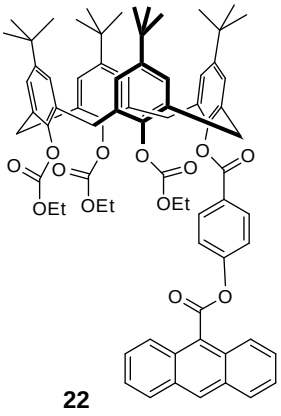

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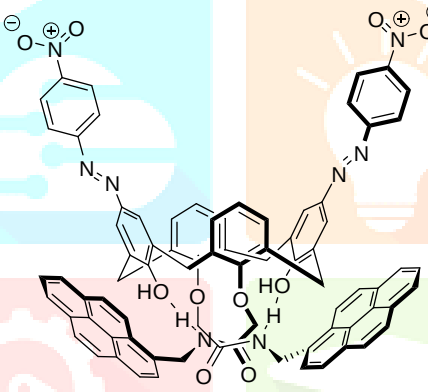
Kim et al.[28] reported that **23** and **24** bearing pyrene as a donor and (*p*-nitrophenyl)azo as an acceptor, show FRET effects. It is believed that the electron transfer from the pyrene units to the nitro groups is partially involved in weakening the emission of **24**. The complexation of



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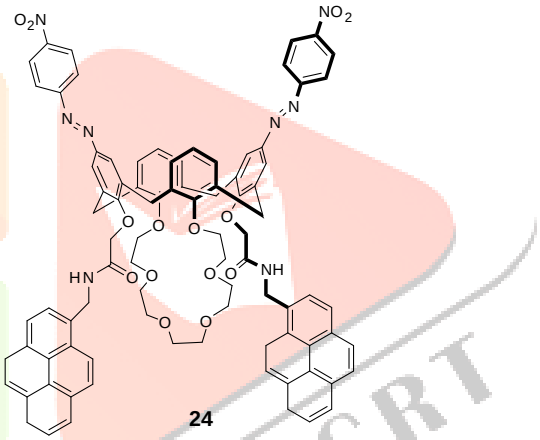

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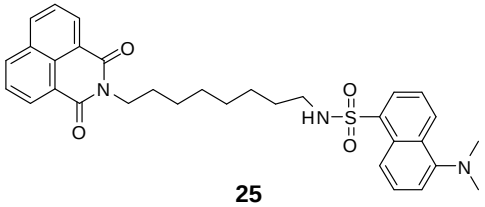
In^{3+} in CH_3CN causes a dramatic red shift of absorption band from 380 to 507 nm, which supports In^{3+} binding to the phenolate oxygen atoms to facilitate the quinone-hydrazone tautomerization. Chemosensor **24** is a FRET-based fluorescent sensor for Pb^{2+}. Due to a significant spectral overlap between the fluorescence emission band of pyrene as a donor and the absorption band of azophenyl unit as an acceptor, chemosensor **24** showed poor fluorescence. On addition of Pb^{2+} to the solution of **24** in CH_3CN caused increase in the pyrene emission. Pb^{2+} induced hypsochromic shift of the azo unit absorption diminished overlap of the donor and acceptor bands, the resulting diminished FRET effect released emission of pyrene.

The solution of dansyl-naphthalimide[29]dyad **25** in 20% acetonitrile containing micelles TX-100 displayed a structured absorption band between 340-350 nm which on addition of Cu^{2+} ions, decreased with concomitant formation of a new band at 284 nm. Also, the intensity of emission spectrum at 525 nm (FRET mediated emission of dansyl moiety) decreased on addition of Cu^{2+} ions with concomitant increase at 375 nm (emission of naphthalimide) by about 12-fold allowing ratiometric estimation of Cu^{2+} ions.



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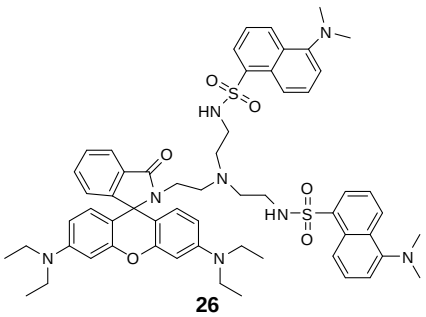

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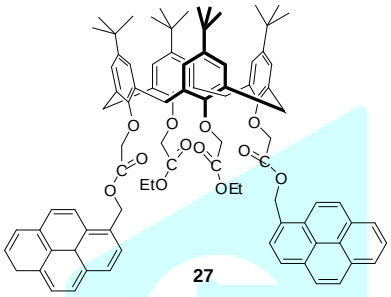
Rhodamine-dansyl[30] chemosensor **26** showed Cu^{2+} induced FRET OFF-ON behavior.The solution of **26** in H_2O-CH_3CN (1:9) gave two absorption bands at 560 and 335 nm due to rhodamine and dansyl moieties, respectively and a strong emission at 507 nm allowing an excellent overlap of acceptor absorption and donor emission. On addition of Cu^{2+} ions to the solution of **26** opened the spirolactam ring of the rhodamine to give FRET based fluorescence enhancement at 580 nm.

2.4 Excimer/exciplex

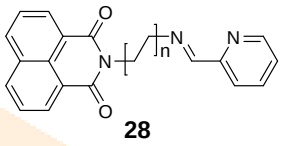
An excimer is defined as a complex formed by the interaction of a fluorophore in the excited state with a fluorophore of the same structure in the ground state. Likewise, if the fluorophore in the excited state is different from the fluorophore in the ground state, the resulting complex is called an exciplex. The emission spectrum of an excimer/exciplex is red-shifted compared with that of the monomer, and a dual emission from the monomer and excimer/exciplex is often observed simultaneously. Therefore, excimer/exciplex formation or dissociation upon interaction with a guest species results in sensing simply by monitoring the excimer/exciplex band. However, there are only a few examples of chemosensors that function based on exciplex formation.

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[31,32]. In molecules with two (or more) pyrenyl substituents, excimer formation can be efficient but is also sensitive to even subtle conformational change, 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.

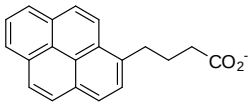
Calix[4]arene derivative **27** wasone of the first reported calixarenes showing excimer formation.[33] The fluorescence spectrum of **27** showed a dual emission with the excimer at ca. 480 nm and the monomer at 390 nm in 4:1 ratio. On addition of Na^+, the I_E:I_M ratio was altered by a change in the relative configuration of the two pyrene moieties induced by the reorientation of the four carbonyl groups of **27** to bind Na^+ ion. Addition of a 100-fold excess of another alkali-metal ion produced at most an 11% change in the ratio in the case of K^+ and a <1% change for Li^+, Rb^+, and Cs^+, showed that **27** may be useful to selectively sense Na^+ ion.



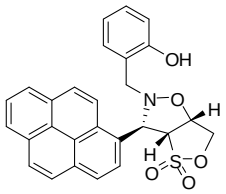
27



28



29



30

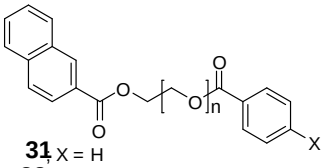
Chemosensors **28**[34] (n = 3–5) on addition of Zn^{2+} and Cd^{2+} exhibited an additional long-wavelength emission due to the excimer formation. Compound **28** (n=2) did not show excimer band, due to limitations of the short connecting chains.

Chemosensor **29**[35]on addition of Zn^{2+} formed 2:1 complex with enhanced excimer emission and permited ratiometric detection of Zn^{2+}. Chemosensor **30**[36]in 50% aqueous ethanol exhibited excimer emission band on addition of Ag^+. Transition metal ions quenched the monomer fluorescence, but with no enhancement in the excimer emission. The lack of excimer emission with Ag^+ in aqueous solutions with > 70% ethanol suggested that hydrophobic stackingof the pyrene units was important.

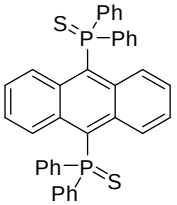
In the presence of Ca^{2+} and Ba^{2+}, chemosensors **31-34**[37]exhibited intramolecular exciplexes in acetonitrile. Chemosensor **34** displayed the largest FE and selectivity for Ca^{2+}. The length of the polyether spacer was chosen to form a suitable podand receptor for these alkali earth cations, with the carbonyl oxygens also playing a ligating role.

Chemosensor **35**[38]derivative exhibited a significant FE in the solid state when exposed to toluene, but not with any other organic solvent including benzene. Its X-ray crystal structure showed it to have a groove suitable for binding toluene by a C–H/π interaction, which allowed exciplex formation.

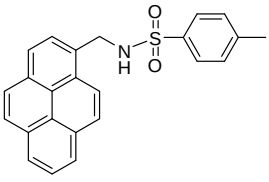
Pyrenylalkylamine **36**[39] in CH_3CN-H_2O (1:1) displayed an intensive absorption band at 342 nm, which became broadened and red-shifted upon the addition of Cu^{2+} ions due to intermolecular π-π stacking dimerization of the two pyrenes in the ground state.Also, the pyrenyl monomer emission of **36** at 375 nm declined with concomitant pyrene excimer emission at 455 nm in the presence of Cu^{2+} ions.



31; X = H
32; X = Cl
33; X = CF3
34; X = CN



35



36

In conclusion, there are number of sensing mechanisms available for chemsensors in literature. Besides these mechanisms, some mechanisms based on fluorescence changes via conformational restriction like aggregation-induced emission (AIE) and C=N isomerization, and excited-state intramolecular proton transfer (ESIPT) have also been investigated[40].

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