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Review article

Fluorescent Compounds Having the Spaced and Integrated Type Receptors

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ABSTRACT: Fluorescent receptors have gained much attention because of their usefulness in analysis and clarification of the roles of biomolecules in living systems. Molecular structures of the functional fluorescent receptors are either a spaced type or an integrated type including that the receptor itself is fluorescent, and play an important role in having the functionality or selectivity of the fluorescent compounds. These spaced type fluorescent receptors are required to have special molecular design in order to transmit the information of molecular recognition to the fluorescent unit through the spacer unit. Compared with the spaced type fluorescent receptors, number of the integrated type receptors is limited due to the difficult molecular design and synthesis. Modification or alteration of the fluorophore frequently caused deterioration of the fluorescent property. Various spaced type and integrated type fluorescent receptors including switch on-off receptors are introduced in this article.

INTRODUCTION; The term "fluorescence" was coined by Stokes[1] from "fluor-Spar" in 1852. He also proposed the "Stoke's theory"[1] which states that the wavelength of fluorescence is greater than the wavelength of the exciting radiation**.**

Only a few fluorescent substances were known at the time that Stoke's theory was presented. Between the end of the 19th century and the beginning of the 20th century, fluorescent organic compounds such as series of acridine, xanthene and others were extensively synthesized (Fig. 1).

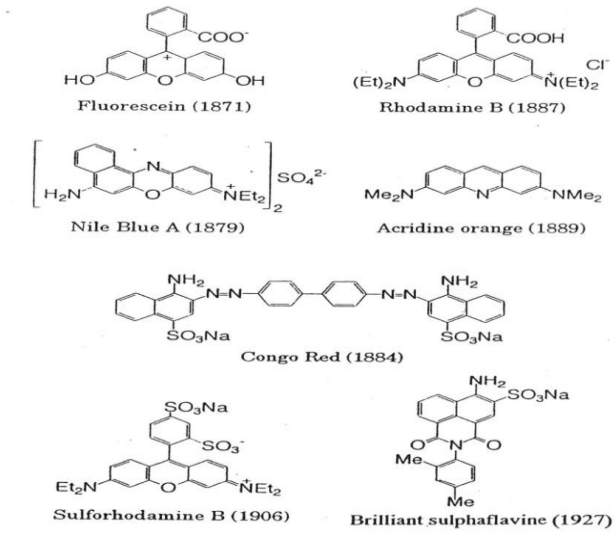

Fig.1. Examples of fluorescent dye. The number in parentheses shows the year that the dye was first synthesized.

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After it turned the 20th century, instrument for measuring luminescence was markedly improved, and physical study and quantum theoretical studies of the luminescence phenomena, and moreover, the behavior of photoexcited molecules were well progressed.

At the same time, analyses that utilize fluorescent phenomena were significantly advanced. It is not clear who first introduced the fluorescence into analytical chemistry, but as early as 1868,[2] trace aluminum was qualitatively analyzed by a green fluorescence of aluminum-morin complex, showing that the fluorescence analysis has more than a hundred years of history.

Since fluorescent analysis utilizes intrinsic photo-luminescence of a substance, specific, selective, and highly sensitive microanalysis can be carried out. There are two classes in application of fluorescent compounds. One is a fluorescent quantitation monitors used as a tracer[3-5] and for quantitative analysis.[6,7] The other is a fluorescent probe.[8,9] It is used for analyzing microenvironmental change, molecular dynamics, molecular orientation, and distance between molecules *etc*.[10] The use of fluorescent dyes for *in situ* analysis has also been developed in clinical and physiological studies.[11-13]

In these days, application of fluorescent dyes to opto-electronics material has been studied extensively.[14,15] Dye laser (Fig. 2) is one of the most successful example, and is used in various fields. Another recent focus of application is organic electroluminescence,[16] which has been studied for over a decade.[17,18] Fluorescent receptors, which utilize fluorescence change induced by intermolecular interaction, have also been a recent main topic.[19]

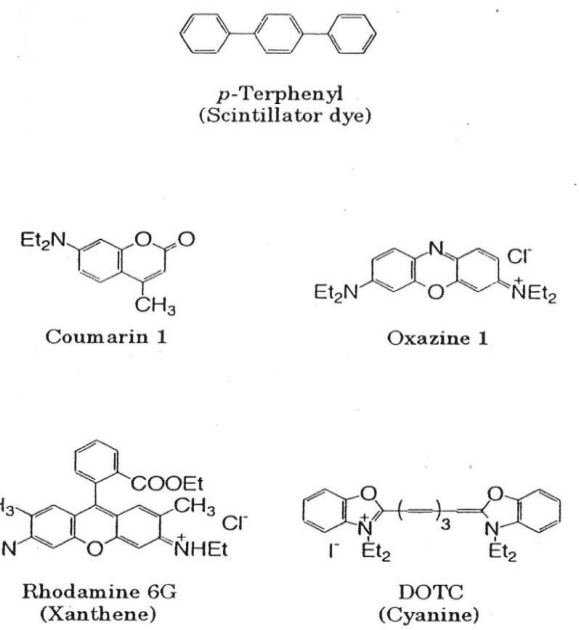


Fig.2. Examples of laser dye.

Receptors in biological systems show not only efficient and specific molecular recognition but also effective response simultaneously or subsequently. Thus, host molecules that have built-in signaling function in their molecular structure have been extensively studied in order to design artificial receptors.

Several methods have been used for analyzing the host-guest binding. ^{1}H-NMR spectroscopy is the most common method. Change of proton chemical shifts offers useful and important information for studying the structure of the complex. However, ^{1}H-NMR spectroscopy cannot be used for *in situ* and real-time analysis, and moreover, it requires more than 10^{-3} mol dm^{-3} of concentration of a sample solution. Detecting the host-guest binding by absorption spectral change is more sensitive, but the concentration down to 10^{-5} mol dm^{-3} is a limit, in general. Signaling by fluorescence has high sensitivity, potentially down to 10^{-9} mol dm^{-3}, and is easily detectable. Therefore, designing and synthesizing the functional fluorescent materials has drawn considerable interest in these days.[20,21]

Molecular structures of the functional fluorescent receptors are either (a) a spaced type[22,23] or (b) an integrated type[24] including that the receptor itself is fluorescent (Fig. 3).[25]

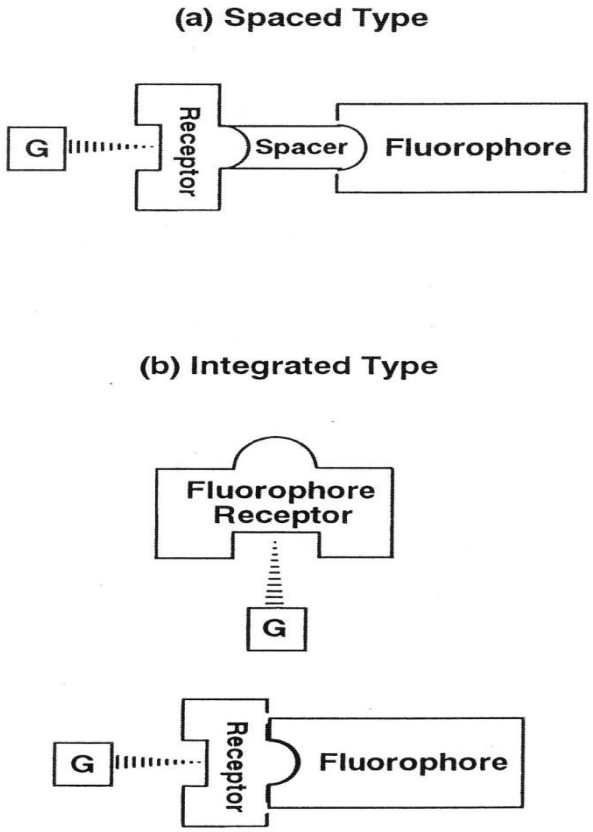


Fig.3. Two different ways of connecting fluorophores and receptors

Spaced type fluorescent receptors

As shown in Fig. 3 (a), these spaced type fluorescent receptors are required to have special molecular design in order to transmit the information of molecular recognition to the fluorescent unit through the spacer unit. Recently, many spaced type fluorescent receptors have been developed, and the numbers are increasing year by year showing severe competition all over the world.

The binding isotherms involving several hydrogen-bonded arrays[26] such as (a) of Fig. 4 have been quantified by means of the fluorescence changes that accompany the binding processes.[27] Small but significant emission wavelength shifts were induced by the barbiturate guest. While most of these studies have been conducted in noncompetitive media like chloroform, the observation of hydrogen-bonded arrays within surfactant micelles in aqueous solution[28-30] bodes well for the future. In an interesting departure, self-assembling monolayers(SAM) of alkanethiols on gold surfaces have been elaborated into relatives of (a) of Fig. 4.[31]

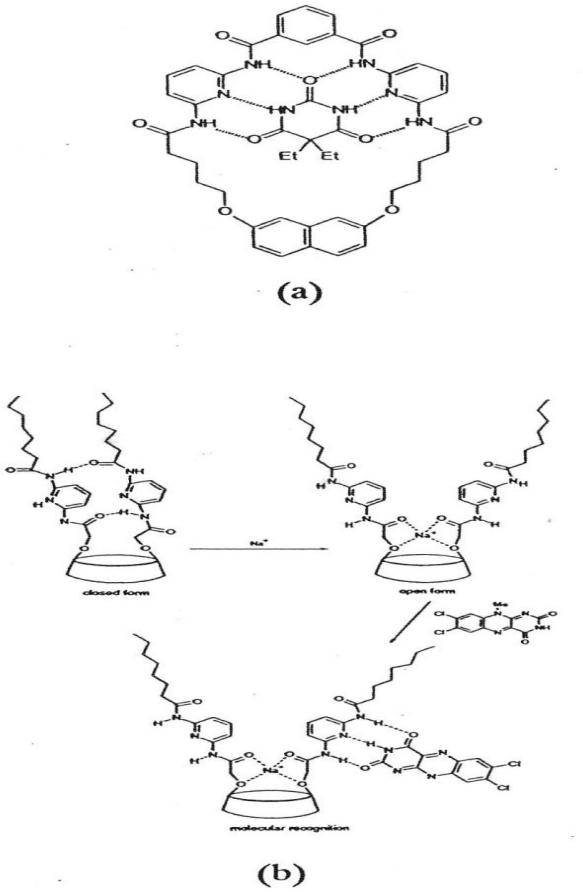


Fig.4. Spaced type macrocyclic fluorescent compounds with ICT excited states

A macrocyclic receptor having calix[4]arene unit (Fig. 4 (b)) employs an indirect but clever approach to the fluorescent sensing of Na^+.[32] Binding of Na^+ to the receptor breaks the internal hydrogen-bonding array and allows the diaminopyridine moieties to reorientate toward an external flavin. Formation of hydrogen bonds induced marked deactivation of the ICT (intramolecular charge transfer) excited state of the flavin. Such hydrogen bond-induced deactivation is known for flavins,[33] pyridylindoles,[34,35] and other fluorophores having the ICT excited state.[36] In this case, the diaminopyridine unit is the spacer, and is connected to flavin, the fluorophore, by intermolecular hydrogen bonds.

Next, there is a wealth of metal complex-based lumophores with MLCT (metal to ligand charge transfer) excited states[37-41] which can be harnessed for the design of sensors and switches.

Calcium ion causes a 8-fold enhancement in the luminescence of (a) of Fig. 5 which is half that achieved by protonation of the *N*-arylaza-15-crown-5 ether receptor.[42] The rationalization of the low luminescence quantum yield and lifetime is the evolution of the Re(I) to bipyridine MLCT state into a nonemissive arylazacrown to bipyridine LLCT (ligand to ligand charge transfer) state. Potassium causes a 3-fold drop in luminescence lifetime of (b) of Fig. 5 upon nestling in the central cavity.[43]

The reasons for this effect is currently unknown. More detailed examination of guest-induced spectral shifts and lifetime effects in this family would be welcome from a sensor perspective. Sodium binding of (c) of Fig. 5 causes blue-shifts in emission spectra even though the alkali metal cation would be expected to electrostatically stabilize the MLCT excited state if sufficient charge is transferred into the receptor-functionalized bipyridine moiety.[44]

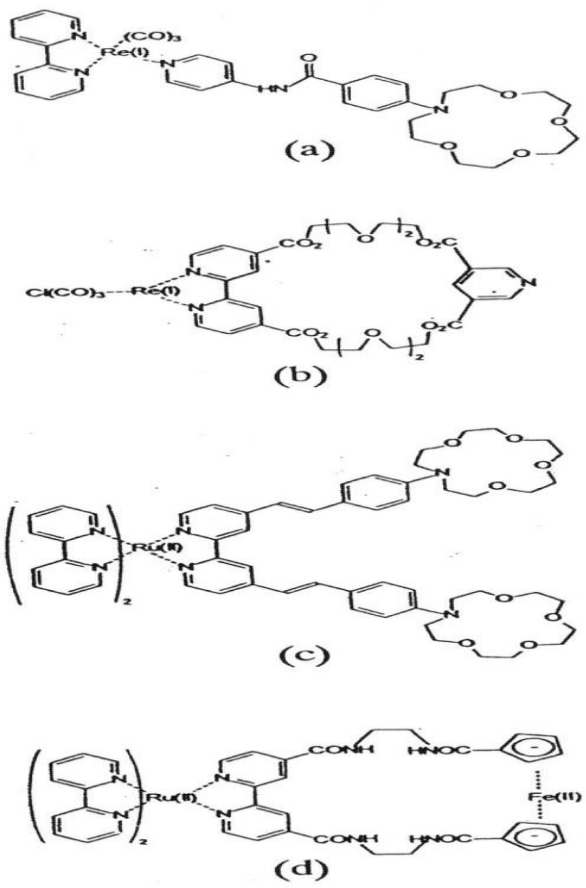


Fig.5. Spaced type fluorescent compounds with MLCT excited states

In the case of compound (d) of Fig. 5, chloride-ion binding to macrocylic cavity serves the switching-on of the luminescence from the MLCT excited state of Ru(II) center, although the mechanism remain to be elucidated. It is particularly interesting in several aspects.[45-47] First, the macrocyclic receptor permits effective selection of Cl^- against the larger $H_2PO_4^-$. Second, the ferrocene moiety distal to the tris(2,2'-bipyridyl)ruthenium(II) can encourage photoinduced electron transfer (PET) or electronic energy transfer (EET) which the Cl^- guest can mediate. Third, the Cl^--induced switching on of luminescence is remarkable, though quantum yield remains low and the spectral shape is anomalous.

Fluorescent signaling via PET system have been intensively studied due to its central role in photosynthesis.[48-53] *N*-Benzannelated cryptand (a) of Fig. 6 produces order of magnitude fluorescent enhancements with K^+.[54] The acetylcholine-responsive (b) of Fig. 6 is an example of a fluorophore with an ICT excited state switching its environment from inside to outside of a resorcin[4]arene receptor upon guest inclusion.[55] The binding of acetylcholine is driven by cation- interactions.[56] The fluorescence is enhanced 2-fold even though the corresponding intermolecular analog (which is less useful as a sensor) gives a more visually dramatic response in alkaline solution. Compound (c) of Fig. 6 is an effort by Sessler to arrange PET from the central porphyrin unit to a benzoquinone guest held by hydrogen bonds to one of the calix[4]arene phenol arrays.[57] However, the weakness of the association leads to a large dynamic contribution to the guest-caused quenching of porphyrin emission. Hunter's (d) of Fig. 6 provides a nice bridge between the hydrogen-bonded ensembles and metal ion-ligand PET systems.[58] The cyclophane holds the benzoquinone guest in its cavity with the aid of hydrogen bonds involving the amide moieties and also accommodates an exomacrocyclic guest, the porphyrinzinc(II) fluorophore, via coordination to one of its pyridine units. Both the PET partners are assembled on the cyclophane scaffold in an orthogonal fashion. Substantial quenching of fluorescence within the termolecular complex is the satisfying observation. Silver ion kills the porphyrinzinc(II)-based emission of the tetramacrocyclic (e) of Fig. 6.[59] Porphyrinzinc(II) fluorescence also suffers at the hands of Eu(III) held in a neighboring 15-crown-5 ether.[60] Along with PET, EET (electronic energy transfer), and heavy atom induced spin-orbit coupling[61] are likely contributors to the switching off effect of the metal ions on the fluorescence.

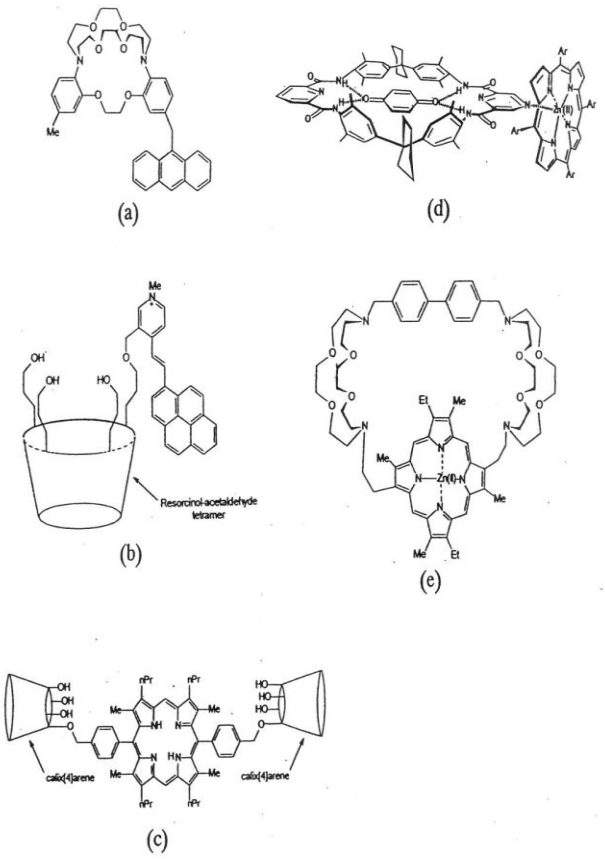


Fig.6. Spaced type fluorescent compounds with PET excited states

In the beginning of 1970, it has been paid attention to biomimetic chemistry which is realized the high bio-function by the molecular recognition.[62] One of those results goes to Still's sequence-selective peptide detection by synthetic small molecules (Fig. 7).[63] Small organic sensor molecules were prepared to bind and signal the presence of unlabeled tripeptides in a sequence-selective manner. When the tripeptides as guest bind to the synthetic receptors, the fluorophore situated inside of the cavity is opened from the latter and it results in enhanced fluorescence as 300-500%. Here, chemosensor **1** selectively binds one tripeptide sequence, (D)Pro(L)Val(L)Gln, for every ~1600 sequences in the library at a concentration of 10 M. Chemosensor **2** was somewhat less selective (binding one tripeptide sequence, (L)Gln(D)Asn(L)Gln, per ~400 sequences). With the chemosensors described here, enhancements are large enough to be readily visible to the naked eye. These sensors were sensitive enough to detect unlabeled cognate peptides both in organic solution and in the solid state at low micromolar concentrations.

In addition, Schneider synthesized the water-soluble peptide receptors as a sequence-selective evaluation of peptide side-chain interaction (Fig. 8).[64] He designed host compounds with one binding site A for the peptide *N*-terminus, and another site B for the *C*-terminus. The structure should ensure that A and B will not interact with each other in order to avoid self-association. The choice was a 18-crown-6 ether for site A, which is well-known to complex protonated nitrogen groups; for site B a peralkylammonium group

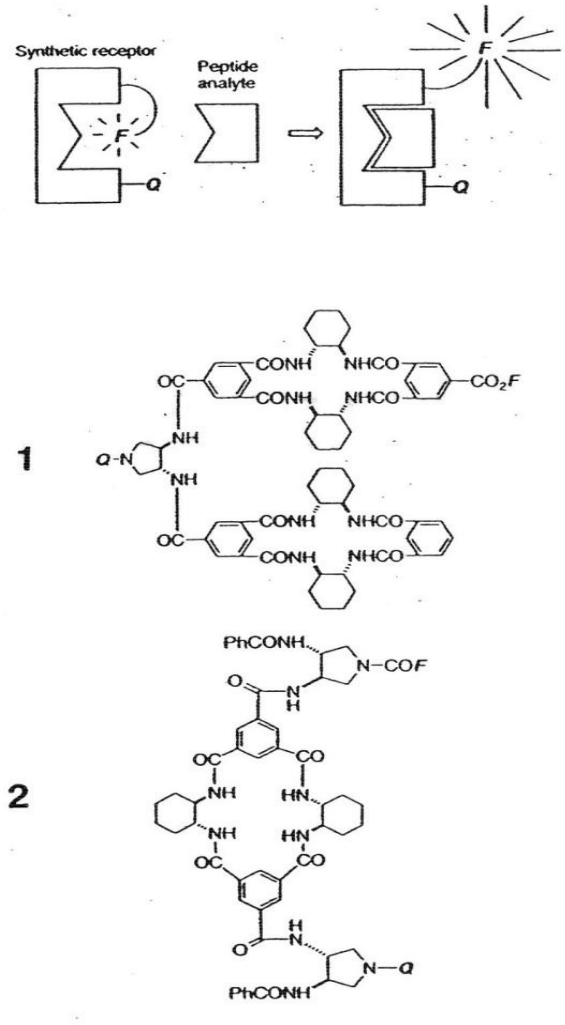


Fig.7. Functionalized chemosensors. ***Q*** is $COC_6H_4N{=}NC_6H_4NMe_2$ and ***F*** is $(CH_2)_2NH\text{-}SO_2C_{10}H_6NMe_2$ (Me, methyl; Ph, phenyl)

was introduced, which has been checked for the absence of any measurable interactions with crown ethers. Introduction of a dansyl (5-(dimethylamino)naphthalene-1-sulfonamide) substituent as the fluorophore yielded the receptor, which not only provides for the convenient analysis by fluorescence but also allows for the first time the evaluation of lipophilic interactions of specific amino acid side chains. The complex with a specific amino acid and its position in the peptide is characterized not only by differences in the association constants but also by changes in the intrinsic fluorescence emission intensities I_{max}/I_0 of the complexes, and to a smaller degree even in changes in the emission maximum wavelength; this can be of interest for the development of corresponding sensors.

Recently, to achieve highly selective binding of Cu(II) within aqueous solution, Imperiali[65] studied the metal binding properties of the amino terminal Cu(II)- and Ni(II)-binding motif found in the serum albumins.[66] These proteins bind both Cu(II) and Ni(II) avidly, with intrinsic affinity constants on the order of 10^{11} M^{-1} for the protein-Cu(II) complex.[67] A family of pentapeptides based on this motif that contain a dansyl fluorophore has been prepared. Addition of Cu(II) or Ni(II) results in efficient quenching, and Cu(II) produces a greater change in fluorescence than Ni(II) (Fig. 9). Furthermore, 100 M concentrations of Mn(II) or Co(II) and millimolar levels of Mg(II), Ca(II), Zn(II), or Cd(II) have no effect on the fluorescence of these chemosensors.

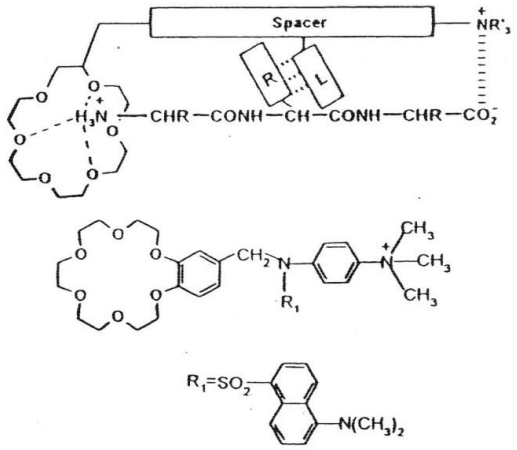


Fig.8. Design and structure of water-soluble peptide receptors

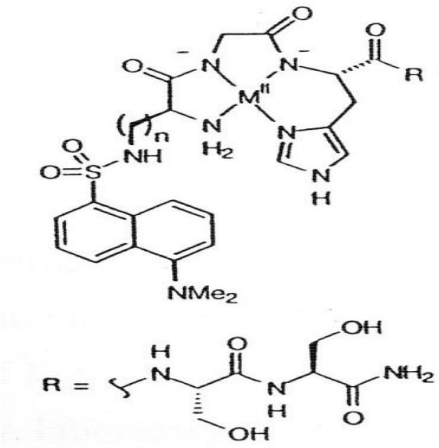


Fig.9. Proposed metal binding geometry of the Cu(II) and Ni(II) receptor

Integrated type fluorescent receptors

Compared with the spaced type fluorescent receptors as depicted above, number of the integrated type receptors is limited due to the difficult molecular design and synthesis. Modification or alteration of the fluorophore frequently caused deterioration of the fluorescent property.

Relatively a few has been known as to the receptor whose recognition site is a fluorophore. An elegant example which employs covalent but reversible interactions is (a) of Fig.10.[68]

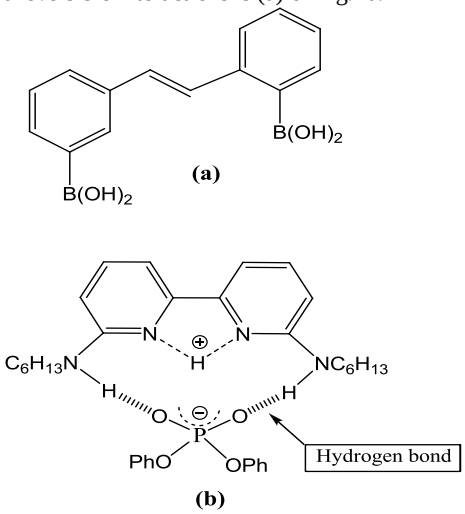


Fig.10. Receptors including the fluorescent properties

This compound switches "on" its fluorescence upon rigidification via macrocyclization with disaccharide guests. Recently, novel fluorescent compound, (b) of Fig. 10 (Hx2), was developed in my laboratory.[25] The host Hx2 showed high selectivity for diphenyl phosphate (DPP) with large binding constant ($K = 10^4 - 10^7$ dm^3 mol^{-1}), showing blue fluorescence in the absence of DPP and green fluorescence on association with DPP.

Other example of the integrated type fluorescent compounds is shown in Fig. 11. Typical molecular design is shown as (a) of Fig. 11, in which the cation acceptor is attached to the electron-deficient terminal of the fluorophore.[69] Cation binding to the acceptor induced red-shift of the emission, presumably by stabilizing ICT excited state from dimethylamino group to the phenyl unit. Lariat ether (b) of Fig. 11 has a stilbene unit that can undergo cis-trans photoisomerization, and shows several interesting features such as cation-controlled absorption spectral change and photocontrollable cation binding.[70]

The integrated type (c) of Fig.11 was designed as the fluorescent probe for metal ions in my laboratory.[71] This compound exhibits a strong fluorescence, whose emission maximum and intensity are modulated upon addition of alkali metal ions. In addition, the integrated type (d) of Fig. 11 was designed as a fluorescent host for monitoring multiple hydrogen-bonding interaction directly by ICT emission. The ICT emission increased only when the amide of the aniline side and the quinoline ring was fixed in the same plane by multiple hydrogen bond formation with cytosine-like guest molecules.[72]

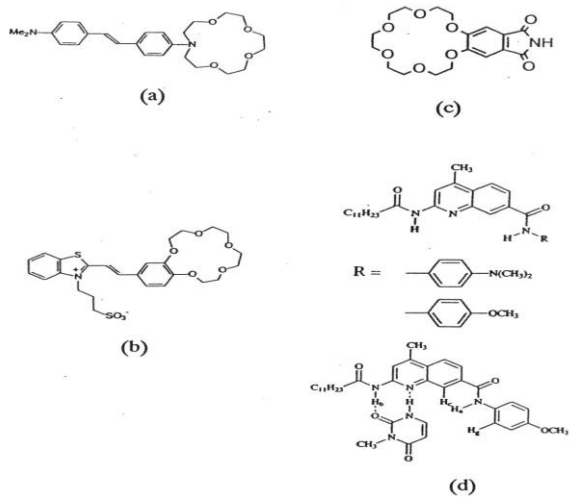


Fig.11. Integrated type fluorescent compounds with ICT excited states

As a integrated type fluorescent compound (Fig.12), we reported recently that 7-(4-methoxybenzoylamino)dipyrido[3,2-a:2',3'-c]phenazine (7-(4-mba)dppz) has a relatively high fluorescence quantum yield (Φ=0.24) comparable to that of the 7-aminodipyrido[3,2-a:2',3'-c]phenazine (7-amino-dppz) (Φ=0.21), despite being a nonrigid π-conjugated system. The photophysical properties of 7-(4-mba)dppz (**1**) as a ligand in the presence of different metal cations (Mg^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) were investigated in acetonitrile solution in view of potential application as the metal ion sensor. when it was plotted as the complexation ratio related to [Zn^{2+} ion]/[**1**] at the emission wavelength 480 nm, the result was the same as the ratio [Mg^{2+} ion] : [**1**] = 1 : 2. Furthermore, when it was plotted as the complexation ratio related to [Ni^{2+} ion]/[**1**] at the emission wavelength 454 nm, the result was shown as the ratio [Ni^{2+} ion] : [**1**] = 1 : 2. For Cu^{2+} ion, the result was the same as the ratio [Ni^{2+} ion] : [**1**] = 1 : 2. Interestingly, we found that all the complexation ratio were the same as [M^{2+} ion] : [**1**] = 1 : 2, as shown in Fig.12 . We suggested from the above results that 7-(4-mba)dppz (**1**) can have a potential application for the cation sensor material such as divalent Ni^{2+} and Cu^{2+} metal ions.[73]

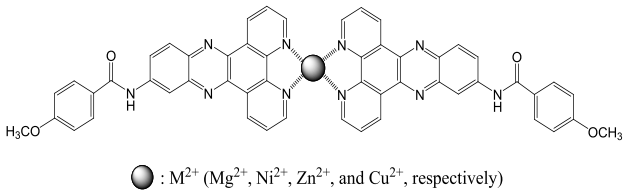


Fig.12. Integrated type fluorescent compound with the complexation as [Metal ion] : [**1**] = 1 : 2

In recent years, fluorescent probes for the detection of environmentally and biologically important metal cations have received extensive attention for designing and development of fluorescent chemosensors.

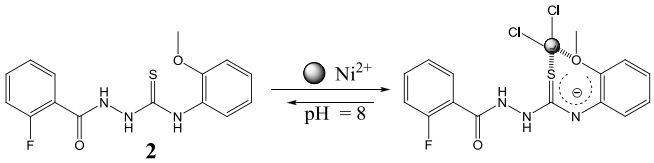
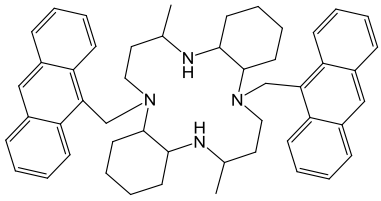


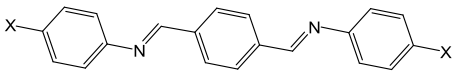
Fig.13. The proposed chelation mechanism of ligand **2** upon $NiCl_2$ addition in acetonitrile/water(1:1,v/v) media

Lee's group reported the photophysical results of 2-(2-fluorobenzoyl)-N-(2-methoxyphenyl)hydrazinecarbothioamide (**2**) functionalized as Ni(II) sensor in micromolar concentration level. Through fluorescence titration at 488 nm, they were confirmed that lignad (**2**) showed the remarkable emission by complexation between ligand (**2**) and Ni(II) while it appeared no emission in case of the competitive ions (Cr^{3+}, Fe^{2+}, Co^{2+}, Ba^{2+}, Cu^{2+}, Ca^{2+}, Na^{+}, K^{+}, Cu^{+}, Cs^{+}). Furthermore, the nontoxic behavior of ligand (**2**) and its ability to track the Ni^{2+} in living cells suggested its possibility to use in biological system as nickel sensor (Fig. 13).[74]

As shown in Fig.14, we simply designed tetraaza macrocycle having the known fluorophore, anthryl group, as both arms and synthesized the novel fluorescent receptor, 3,14-dimethyl-6,17-N,N'-di(9-methylanthryl)-2,6,13,17-tetraazatricyclo[14,4,$0^{1.18}$,$0^{7.12}$]docosane (macrocycle **L**).[75] The macrocycle L is the novel fluorescent receptor having the switching ability by the external stimuli as well as having the recognizing ability of various metal ions. In particular, macrocycle L shows the possibility of the selectivity of metal ions even in the same charge ions of a different metal, and the values of association constant (M^{-1}) of that for metal ions are consistent with the tendency of increasing charge number of metal ion. Furthermore, as shown in Fig.15, this macrocycle L exhibited a switch on-off behavior through the fluorescent responses by aromatic imine molecule(X=H)/trifluoroacetic acid(TFA). In the "switch on" state, it was supposed that the aromatic imine molecule is in the cavity of macrocycle L and a photoinduced electron transfer (PET) from the nitrogen of azacrown part to the anthryl group is inhibited by the interaction between the aromatic imine molecule and the azacrown part of macrocycle L. In the "switch off" state, it was supposed that the protonated imine molecule is induced by the continuous addition of TFA and a repulsion between the protonated azacrown part and the protonated imine molecule is occurred. It was considered that this process induces the intermolecular PET from the protonated imine molecule to the anthryl group of macrocycle L because of a proximity effect between the anthryl group and the protonated imine molecule.



macrocycle L



aromatic imine molecule
X = H, CH_3, Cl, $N(CH_3)_2$, OCH_3 and F

Fig.14. The structure of macrocycle L and aromatic imine molecules

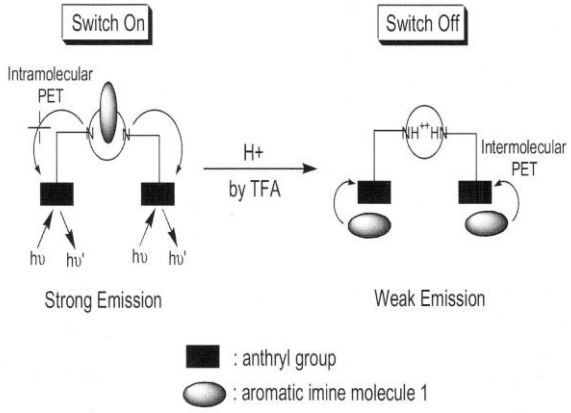


Fig.15. The proposed scheme of the switch on-off

CONCLUSION

In recent years, the development of fluorescent receptors has been attracted and competed because those are useful to analyze and clarify the roles of biomolecules in living systems, and applicated in the construction of switching systems for the molecular electronic/photonic devices as well as in the stoichiometric host-guest recognition as an ionic and molecular sensing. Furthermore, the novel fluorescent receptor having smart and multi-functionality is attracting further research interest. Herein, two kinds of receptor including switch on-off types were described in this review article. Various spaced type and integrated type receptors were introduced and appeared as MLCT, ICT, EET or PET excited states. These fluorescent receptors showed effectively the novel functionality or selectivity such as metal ion sensing and molecular recognition in the micromolar level.

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KEY WORDS

Fluorescent compounds, Spaced type, Integrated type, Fluorescent receptor, Fluorophore, Complexation, Intramolecular charge transfer, and Photoinduced electron transfer

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