24. XANTHENE-BASED FLUORESCENT CHEMOSENSOR (REVIEW)

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Chemosensor is a sensory sensor that transduces a chemical signal into an action potential. Fluorescence measurement of specific molecules by artificial chemosensors is a versatile technique offering utility not only for in virto assays but also in vivo imaging studies using fluorescence microscopy. So it is necessary to develop efficient sensors for recognition and detection of metal ions either in aqueous environment or in living cells/organism. I selected reports about Xanthene based chemosensor for Hg^{2+} because rhodamine(derivative of xanthene) has long absoption and emission wavelengths, large absoption coefficient and high fluorescence quantum yield. Fisrt one is chemosensors for Hg^{2+} using a Rhodamine-cyclen compound by Yasuhiro Shiraishi. Second one is chemisensors for Hg^{2+} using a new Rhodamine-based chemosensor RBSN by Peng Zhou. The last one is chemosensors for anions using a Xanthene-based Zn complex by Itaru Hamachi.

Key Words : *Chemosensor, Xanthene, Rhodamine,fluorescence,* Hg^{2+}

1. BACKGROUND

Xanthene is a kind of yellow organic heterocyclic compounds. Chemical formula of Xanthene is $C_{13}H_{10}O$. Derivatives of Xanthene are used in the basis of a class of dyes which includes fluorescein, eosins and rhodamines. Because the derivatives of xanthene can be fluorescent from yellow to red which it is easy to tell by naked eyes. It is used electronic material and chemical sensor by using brilliant dyes.

During the past few decades, much effort has been devoted to the development of fluorescent chemosensors such as Hg^{2+} metal ions. However, the results of most sensors are fluorescence quenching response and low fluorescence enhancement. But Xanthene chemosensors show high selective and intensity . Compared to early reported xanthene based Hg^{2+} sensors, the fluorescence enhancement of Rhodamine-cyclen compound by Yasuhiro is more higher .

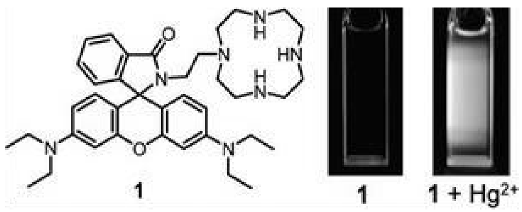


Fig.1 A rhodamine and Hg^{2+} reaction (Ref1)

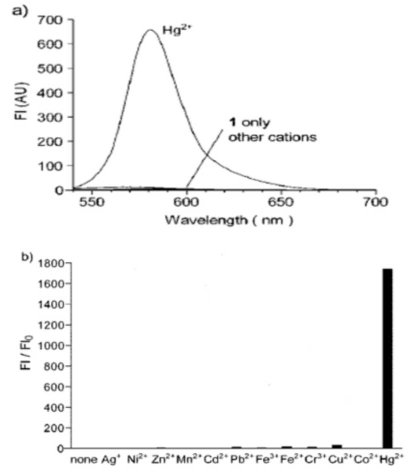


Fig. 2 (a) Fluorescence spectra (λ ex) 530 nm) of 1 (50 μ M) measured in CH_3CN with respective metal cations (b) Fluorescence enhancement factor of 1.(Ref.1)

2. CHEMICAL SENSOR

(1) Rhodamine-cyclen compound

A number of useful sensors for Ca^{2+},Zn^{2+}, Hg^{2+},, etc, have

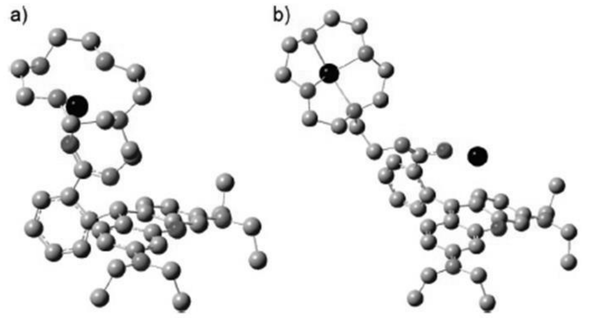


Fig .3 Calculated structures of (a) 1:1 and (b) 1:2 1-Hg^{2+} complexes.(Ref.1)

been designed and are available for imaging studies in living cells.

In Yasuhiro Shiraishi report, he studied Hg^{2+} chemosensor using rhodamines. Rhodamine is a dye used extensively as a fluorescence reagent due to its excellent photophysical properties such as long absorption and emission wavelength, large absorption coefficient, and high fluorescence quantum yield.

A Rhodamine B – cyclen conjugate**(1)** behaves as highly sensitive and selective fluorescent chemosensor for Hg^{2+}. The high emission selectivity is due to the formation of 1- Hg^{2+} 1:2 complex. Due to Spirocycle opening of **(1)**, he found 'turn on' fluorescence.

Yasuhiro Shiraishi studied the enhancement and selectivity of this chemosensor. **Fig.2(a)** shows that without cations, Rhodamine-Cyclen**(1)** shows very weak peak and fluorescence. However, addition of Hg^{2+}, create strong orange fluorescence and peak at 540-670nm. And the fluorescence enhancement factor measured that Hg^{2+} is determined to be 1700, which is the highest value among other metal cations. The fluorescence enhancement factor of Hg^{2+} is more than 50 times of that obtained with other metal cations. As a result, he found that rhodamine-cyclen Hg^{2+} sensor has highly sensitive and selective.

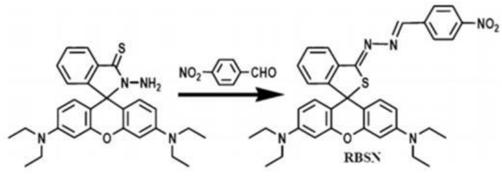
In **Fig.3**, when adding 2 equiv of Hg^{2+}, the coordination of the carbonyl oxygen with second Hg^{2+}. Therefore it leads to spirocycle opening of **(1)**.Consequently, He found that the structure of the 1:2 1-Hg^{2+} complexes has strong fluorescence.

From **Fig.1**,**2**,**3**, he found that a rhodamine B – cyclen conjugate**(1)** behaves as highly sensitive and selective fluorescent chemosensor for Hg^{2+}.

(2) Rhodamine-based chemosensor RBSN

A new Rhodamine-based chemosensor RBSN designed for the selective detection of Hg^{2+} in aqueous.

RBSN is colorless and fluorescence inactive without Hg^{2+}



Scheme 1 Synthetic procedures of compounds RBSN.(Ref2)

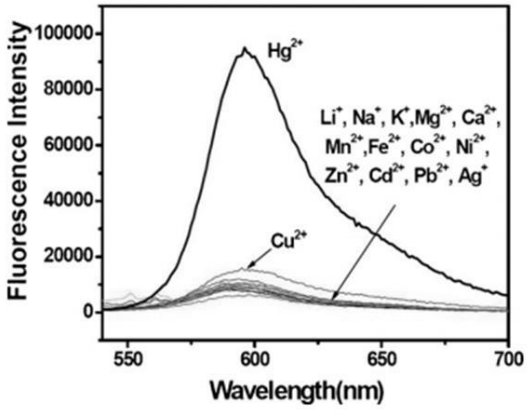


Fig.4 Fluorescence spectra of RBSN in DMF/H2O at pH = 7, in the presence of 50M Hg^{2+}, 25 mM of ther other metal ions (Ref.2)

metal ions. However addition of Hg^{2+} ion to solution, RBSN shows a pink color and a strong yellow fluorescence. The reason of this fluorescence is Hg^{2+}-induced ring opening reaction.

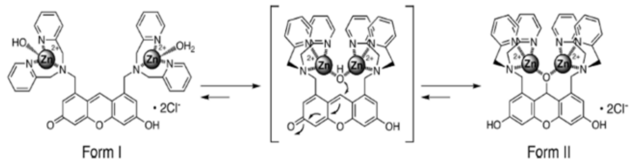
The Fluorescence Intensity of Hg^{2+} is a highly selective and shows dramatic change. Only the addition of Cu^{2+} shows small fluorescence intensity changes. However the other do not change under identical conditions.

(3) Chemosensors for anion

A number of practically useful sensors for Ca^{2+}, Zn^{2+},Mg^{2+},etc., have been designed which are available for imaging studies in living cells and contribute to understanding the physiological roles of cations. In contrast, fluorescent chemosensors for biologically relevant anions have remained a challenging topic. It is difficult to make the design of a binding motif for anionic species that works well in aqueous solution.

In Itaru Hamachi, he report a new fluorescent chemosensor for nucleoside polyphosphates such as ATP using metal-anion coordination chemistry. And the 'turn on' fluorescence of 1-2Zn(II) is based on a new mechanism, which involves the binding-induced recovery of the conjugated form of the xanthene ring.

From **Fig.5**, he found 'turn on' fluorescence sensing mechanism. First, ATP is binding to the two Zn II -Dpa sites. Binding induces the disruption due to multipoint interactions



Scheme 2 Structual Equilibrium of 1-2Zn(II) under Neutral Aqueous conditions(Ref3)

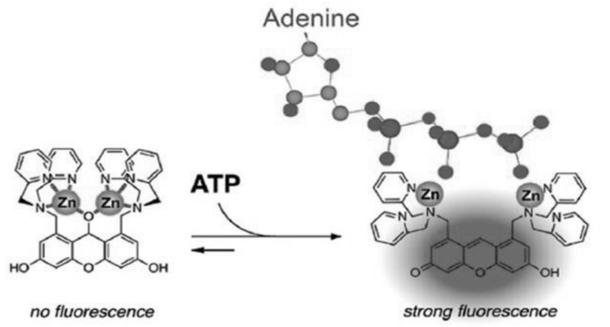


Fig.5 Schematic illustration of the turn on fluorescence sensing mechanism of 1-2Zn(II) for ATP. (Ref.3)

between Zn II -Dpa sites and triphosphates group of ATP. And then oxygen bridges is disrupted. It results in the recovery of the conjugated Xanthene structure. So this structure is showing strong green fluorescence at λ =523nm. As a result, he found that a photograph of the turn on fluorescence of 1-2Zn(II) upon binding to ATP demonstrated the naked eye detection of ATP using 1-2Zn(II)

3. DISCUSSION

I studied the xanthene based chemosensor for Hg^{2+} metal ions written by Yasuhiro Shiraishi and Peng Zhou.

These days, water pollution due to heavy metal is very serious problem around the world. It is important to develop a sensor of cations for water environment. And many efforts are under way to make design mechanism of sensors.

Compared to these two reports using xanthene chemosensor, **Fig.2(a)** shows strong orange fluorescence at 540-670nm. But without cations, it shows very weak fluorescence. Compared to the rate of Hg^{2+} and the other metals, the fluroscence intensity of Hg^{2+} is higher. It is almost 65times.

However the rate of Hg^{2+} is just 9 times higher than others. There from even though they used same xanthene based compound, the higher selectivity was shown with Rhodamine-cyclen compound.

In order to detect Hg^{2+} metal ions, using Rhodamine-cyclen compound can get more propriate results.

In the report of Yasuhiro Shiraishi, he reported the chemosensors for Hg^{2+}. Advandtage of these Hg^{2+} sensors is that a rhodamine B- cycclen conjugate compound behaves as a highly sensitive and selective fluorescent. In fact, in a river or sea, there are a variety of heavy metal. Therefore selectivity is important. But these sensor has limitation that 1- Hg^{2+} 1:2 complex. It seems to be difficult to use useful and easily

And during the past few decades, much effort has been devoted to the development of fluorescent chemosensor for cations. But the number of reports about anions chemosensor is short. It is difficult to make design and there has been no general design principle for the effective transduction of an anion binding. .

In the the report of Itaru Hamachi, I was interested in selecting ATP because of the fusion of biology and chemistry. Anions play a fundamental role in a wide range of chemistry and biological process. So it should need to be developed. The chemosensor 1-2Zn(II) in this report is selectively senses nucleoside polyphosphates with a large fluorescence enhancement and strong binding affinity. But it is hard to use various other anions. And disadvantage of these sensor is react to deconjugated form.

4. CONCLUSION

I studied chemosensors for Hg^{2+} cations and anion using xanthene based compound. Xanthene based compound has highly selectivity and fluorescene intensity. Even though chemosensors for Hg^{2+} cations used same xanthene based compound, the higher selectivity was shown when we used Rhodamine-cyclen compound. And we can detect not only cations for metal ions but also anions to Xanthene based compound.

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