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Chemosensors Based on Benzothiazole and Coumarin Platform

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ABSTRACT

The development of methods for the translation of fluorophores into fluorescent probes continues to be a robust field for medicinal chemists and chemical biologists, Ideal responsive fluorescent probes are those that contain a fluorophore tethered to both a sensing unit, to ensure selectivity of response, and a targeting group, to control the sub-cellular localisation of the probe. Due to their high levels of sensitivity, fast response time, and technical simplicity, small molecule based fluorescent probes have been widely developed and applied to the detection of many biologically important analytes, in particular, fluorescent probes for biologically and/or environmentally important cations, anions, small neutral molecules, and biological macromolecules. This review highlights the advances in the development of fluorescent and/or colorimetric probes, based on coumarin and benzothiazole platform.

Keywords: Coumarin, Benzothiazole, Fluorophores, Fluorescent Probes

I. INTRODUCTION

Benzothiazole and its derivatives are important heterocyclic compounds and are used in various chemical fields due to their rigid conjugated structure, good optical properties and pharmacological activity, for example, for the construction of fluorescent probes, scale inhibitors and functional molecules, dyes, drugs, sensors, etc., probes have been developed rapidly in the past decade. Compared with traditional analytical techniques, such as titration, chromatography, electrochemistry and chemiluminescence, fluorescent probes can achieve specific detection and rapid response to analytes. The benzothiazole fluorescent probe has the advantages of high quantum yield and large Stokes shift. 2-(2-hydroxyphenyl) benzothiazole (HBT) as a typical ESIPT luminescent agent is an important derivative of benzothiazole The introduction of different electron withdrawing or electron-donating substituents on it will inhibit or promote the ESIPT process of HBT. The benzothiazole fluorescent probes can be further modified by its hydroxyl, hydroxyl ortho, hydroxyl meta and hydroxyl para. The mechanism of benzothiazole fluorescent probes in detecting analytes mainly includes photoinduced electron transfer (PET), excited-state intramolecular proton transfer (ESIPT), intramolecular charge transfer (ICT) and aggregation-induced emission (AIE). Because benzothiazole fluorescent probes contain thiazole ring, they show excellent coordination ability .Benzothiazole fluorescent probes can be used to detect metal ions,

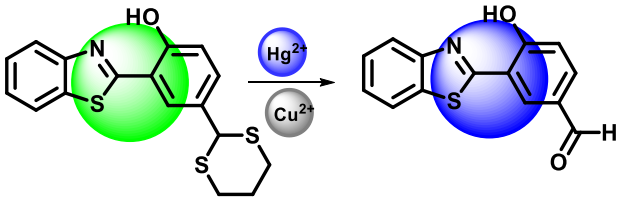
anions, small molecules and biological macromolecules through complexation reactions, hydrolysis reactions, nucleophilic additions, etc., and are used in biological cell imaging and pH sensing. In recent years, research on them has been very active, but there is no review of shaped benzothiazole fluorescent probes. Therefore, in this paper, starting from the type of analyte, it is mainly divided into several categories according to metal ions, anions, small molecules and biological macromolecules. The synthesis methods, optical properties, possible mechanisms and applications of benzothiazole fluorescent probes in the past are reviewed, which provides a reference for the further study of benzothiazole fluorescent probes.

Coumarins as Fluorescent Chemosensors Most coumarin-derived fluorescent chemosensors were built combing the coumarin moiety with other functional receptors. Often, an amino group or hydroxyl at the 7-position and an acetyl group at 3-position have been adopted as the fluorophore scaffold due to the enhanced charge transfer character resulting from this substitution pattern. Somechemosensors are weak fluorophores because of quenching effects such as the photo induced electron transfer (PET) process, isomerization, and other effects. After interactions with their analytes, these quenching effects are inhibited and a strong fluorescence is recovered. Other chemosensors of the chemo dosimeter subclass, rely on chemical bond cleavage, releasing a strongly fluorescent compound or conversely the creation of novel chemical bonds resulting in wavelength changes.

This review introduces the three main light emitting mechanisms (PET, ICT, FRET) of fluorescent probes, and enumerates some probes based on this light emitting mechanism. In terms ofthe synthesis of coumarin fluorescent probes, the existing substituents on the core of coumarin compounds were modified. Based on the positions of the modified substituents, some of the fluorescent probes reported in the past ten years are listed. Most of the fluorescent probes are formed by modifying the 3 and 7 position substituents on the mother nucleus, and the 4 and 8 position substituents are relatively less modified. In terms of probe applications, the detection and application of coumarin fluorescent probes for Cu^{2+}, Hg^{2+}, Mg^{2+}, Zn^{2+}, pH, environmental polarity, and active oxygen and sulphide in the past years are mainly introduced.

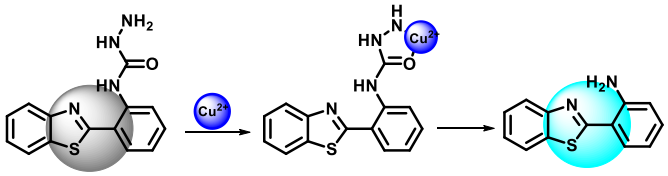
Chemosensors Based On Benzothiazole Platform:

Gu and co-workers[1] designed a highly sensitive and selective fluorescent probe (Scheme 1.) with two different reaction sites, an thioacetal group (Hg^{2+}) and O and N atoms of the benzothiazole dye (Cu^{2+}). The deprotonation of hydroxyl group inhibits the ESIPT process due to the paramagnetic property of Cu^{2+}, causing fluorescence quenching. The probe showed good cell permeability and ratiometric fluorescent response to Hg^{2+} and fluorescence quenching behavior to Cu^{2+}, which induces naked-eye fluorescent color changes from green to blue and colorless, respectively. The LOD of for Cu^{2+} and Hg^{2+} was 2.4 nM and 7.6 nM, respectively.



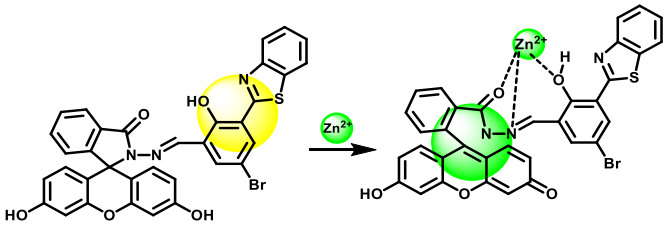
Scheme 1: *Probe for detection of Mercury (II)*

Ryu and co-workers[2] prepared a new Cu^{2+}-selective reaction-based fluorescent probe (Scheme 2) based on the semicarbazide bearing derivative of 2-(2-aminophenyl) benzothiazole. The PET effect caused fluorescence quenching in probe due to the presence of hydrazide part. After the addition of Cu2+, the semicarbazide moiety is hydrolyzed to produce 2- (2-aminophenyl) benzothiazole with strong fluorescence. The detection limit was 1.71×10^{-8} M (1.1 ppb).



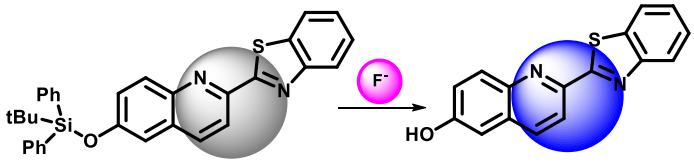
Scheme 2: *Probe for detection of Copper (II)*

Erdemir and co-workers[3] synthesized a novel selective, sensitive, colorimetric and fluorescent fluorescein-based sensor (Scheme 3) that containing benzothiazole unit for highly selective, sensitive and rapid recognition towards Zn^{2+} which causes spirolactam of fluorescein to ring-opening, forming a complex with probe at a stoichimetric ratio of 1:1. The LOD was 5.64 μM in CH_3CN-H_2O (2:1, v/v).



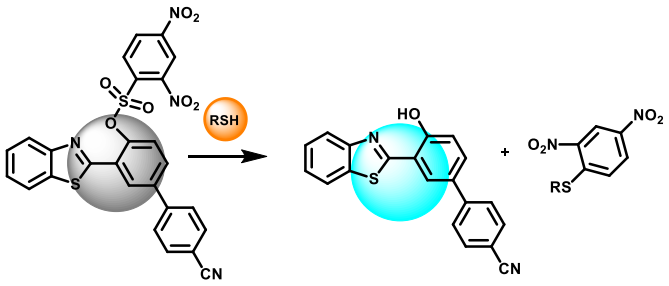
Scheme 3: *Probe for detection of Zinc (II)*

Hu and co-workers[4] designed a TBDPS-containing two-photon fluorescent probe (Scheme 4) for F- detection. Fluoride induced cleavage of Si-O produces highly fluorescent compound 6-hydroxyl-quinonline-2-benzothiazole. When F^- is added, a new fluorescence emission peak at 533 nm develops and responds positively to the F^- concentration by increasing the intensity of the fluorescence. The LOD was 0.5 μM.



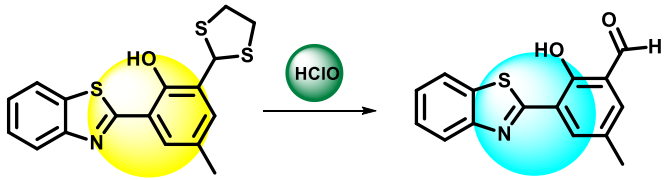
Scheme 4: *Fluoride sensing probe*

Chen and co-workers[5] synthesized probe (Scheme 5) with 202 nm Stokes shift by introducing 2,4-DNBS group. Due to the PET process and the inhibition of the ESIPT process by the 2,4-DNBS moiety an electron acceptor, the fluorophore in the probe was partially quenched. Cleavage of DNBS part eliminated the PET process and restored the ESIPT process, resulting in strong fluorescence at 482 nm The Limit of detection of Cys, GSH and Hcy were 20 nM, 170 nM and 120 nM.



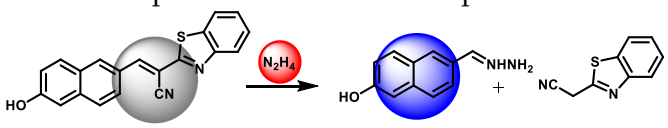
Scheme 5: *Probe for detection of Biothiol*

Chang and co-workers[6] developed a highly selective and ratiometric fluorescent probe by incorporating a dithiolane functional group (Scheme 6) for hypochlorite detection in living cells. The probe emits yellow fluorescence at 546 nm as a result of the AIE phenomenon. The dithiolane functional group is split after the addition of HOCl, producing an aldehyde group. The ESIPT procedure caused Probe-HClO to glow blue at 460 nm. In the PBS buffer, the Limit of Detection was as low as 8.9 nM



Scheme 6: *Hypochlorous acid probe*

Wang and co-workers[7] developed a two-photon highly sensitive and selective fluorescent probe having 2-benzothiazoleacetonitrile as recognition site for N_2H_4 (Scheme 7) Based on this, a probe can be used to find HeLa cells, gaseous N_2H_4 hydrazine, and fresh rat liver slices with alive tissues. With an excitation wavelength of 360 nm, the probe is essentially non-fluorescent. The probe showed robust emission at 448 nm in PBS-DMSO (v/v=2/1, pH=7.4) at room temperature when N_2H^4 was present.

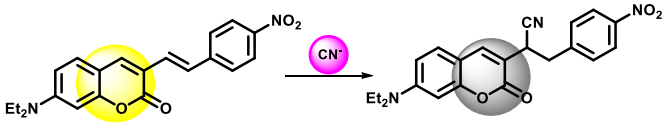


Scheme 7: *Hydrazine Probe*

Chemosensors Based On Coumarin Platform:

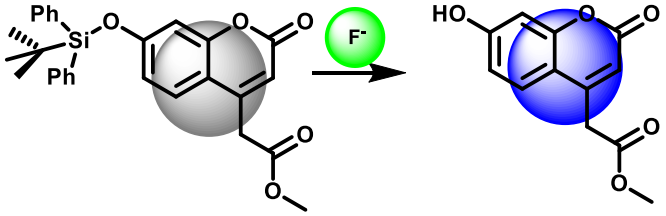
Zhang and co-workers[8] described a coumarin-nitrobenzene conjugate (Scheme 8) highly selective probe for the detection of cyanide in aqueous

acetonitrile solution. Probe displayed considerable dual changes in both absorption (blue-shift) and emission bands for CN-, which could be observed directly with the naked eye. The cyanide addition interrupts the π-conjugation in probe, which obstructs the ICT process and results in a color change from yellow to colorless and a significant fluorescence enhancement at 410 nm. Detection limit 0.14 mM.



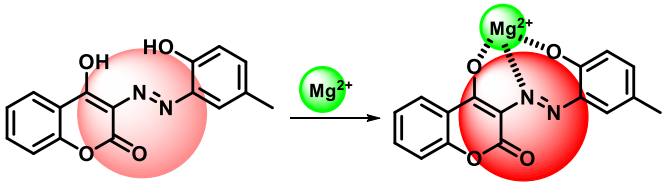
Scheme 8: Probe for detection of Cyanide

Hong and co-workers[9] developed fluoride ion probe with ICT mechanism, based on the derivative of TBDPS-protected 7-hydroxycoumarin. (Scheme 9) This time the sensing can be carried out in pure water buffered by HEPES (pH = 7.4), while the emission enhancement induced by fluoride was recorded to be dependent on time, which required 4h to reach a saturation. The sensor was successfully used for in vitro bioimaging on A549 human lung carcinoma cells, and no cytotoxicity was observed.



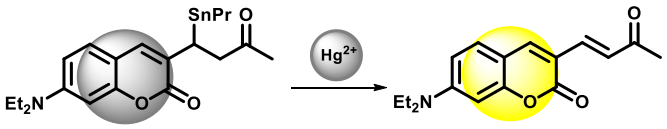
Scheme 9: *Probe for detection of Fluoride*

Mondal and co-workers[10] developed a coumarin azophenol based chemosensor (Scheme 10) for selective detection of Mg^{2+}. Complex of Probe-Mg^{2+} emitted strong red fluorescence as a result of the inhibition of a PET process in the non complexed fluorophore, and the addition of F^- leads to the de-complexation of the magnesium complex, thus quenching the fluorescence due to the restoration of the PET process in the free fluorophore. The chemosensor can even detect Mg^{2+} in the intracellular region of human lung cancer cells.



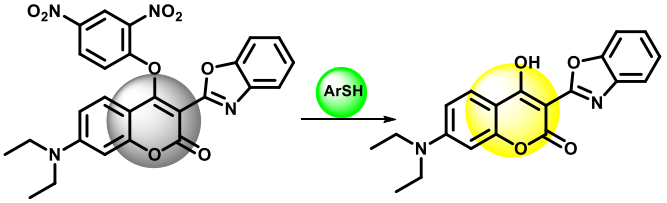
Scheme 10: *Probe for detection of Magnesium*

Wang and Co-workers[11] designed a colorimetric fluorescent probe (Scheme 11) for the highly selective, sensitive and facile detection of Hg^{2+}. Compound fluorescence maximum at 488 and 560 nm before and after a very fast Hg^{2+} promoted desulfurization reaction of thio-ether moiety in an aqueous mixture containing only 0.5% CH_3CN. In the absence of Hg^{2+}, the probe at a concentration of 5.0 mM displayed an emission at 488 nm when excited at 435 nm.



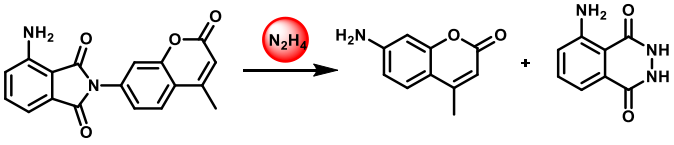
Scheme 11: *Probe for detection of Mercury (II)*

Zhao and co-workers[12] designed a selective and sensitive fluorescent probe (Scheme 12) for hydrogen sulfide based on thiolysis of dinitrophenyl ether moiety. This new easily prepared probe can work efficiently at near neutral pH, and shows a large fluorescence enhancement with distinct color change. A clear color change from colorless (λ=335 nm) to pale yellow (λ=370 nm) could be observed by naked eye (It was also applied to detect H_2S in living cells with clear fluorescence enhancements.



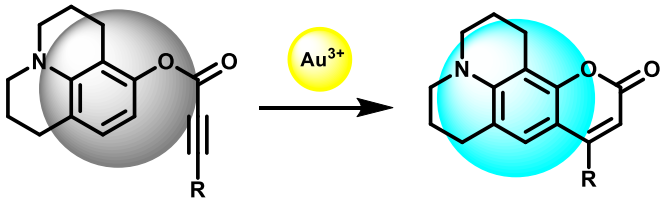
Scheme 12: *Probe for detection of aromatic Thiol*

Ciu L and group[13] developed a coumarin-phthalimide conjugate based (Scheme 13) highly selective probe on colorimetric as well as chemiluminometric signal outputs for the specific detection of hydrazine is characterized by a broad fluorescent band centered at 480 nm, and the addition of hydrazine results in the liberation of 7-aminocoumarin via a Gabriel-type reaction with a characteristic fluorescence emission at 420 nm.The LOD was determined to be 0.1 μM.



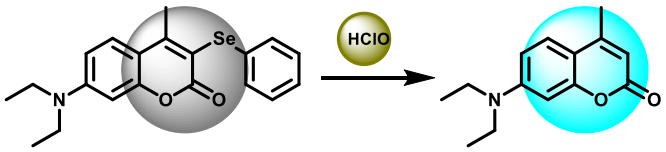
Scheme 13: *Probe for detection of Hydrazine*

Yin's group[14] developed highly selective fluorescent probe (Scheme 14) for detection of Au^{3+}. These fluorogenic sensors require the presence of Au^{3+} to enable an in situ hydroarylation reaction, resulting in the formation of a coumarin, and detection concentration of Au^{3+} was as low as 0.1 mM or less. Fluorescent imaging of Au^{3+} in living cells was also successfully demonstrated. When Au^{3+} is added, a strong fluorescence emission at 511 nm for and at 467 nm.



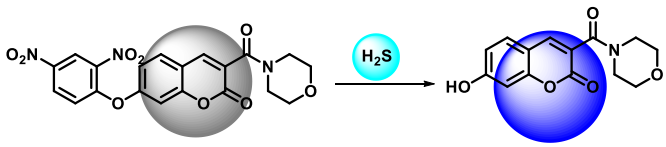
Scheme 14: *Probe for detection of Au (III)*

Li and co-workers[15] on the basis of a specific intramolecular selenoxide elimination reaction (Scheme 15) developed a fluorescent probes for the highly selective and rapid detection of hypochlorite. The probe, was successfully utilized in detecting hypochlorite in aqueous media and living cells similarly used the disruption of conjugation in dihydrocoumarins as a convenient way to quench the fluorescence of the parent coumarin compound, as is apparent from the very low quantum yields.



Scheme 15: *Probe for detection of Hypochlorous Acid*

Ou and Co-workers[16] reported a coumarin based simple "off–on" fluorescent probe (Scheme 16) for selective detection of H_2S , which uses the 2,4-dinitrophenyl group as the reaction site. Due to the PET quenching the probe was non-fluorescent. The probe displayed a quick and significant fluorescence "off–on" response to H_2S, and the limit of detection was 2.31x 10^{-7} M. Additionally the probe could be used for imaging and monitoring exogenous and endogenous H2S in living cells.



Scheme 16: *Probe for detection of H_2S*

II. CONCLUSION

This article reviews the benzothiazole and coumarin based fluorescent probes and is mainly divided into metal ions, anions, small molecules and biological macromolecules according to the type of analyte. Modification of benzothiazole, Coumarin and its derivatives can be used probes for different purposes. Benzothiazole and Coumarin probes combine with analytes through complexation, hydrolysis, nucleophilic addition, oxidation reactions, etc., to change their luminescent properties. The benzothiazole as well coumarin based probe has the advantages of wide linear range and low detection limit, and can be used to quantitatively detect analytes in real water samples.

This review has also highlighted the various aspects of coumarin fluorescent probes, including their chemical synthesis and application. Coumarin derivatives have good applications as fluorescent probes in many fields such as detecting metal ions, environmental polarity, some disease-related active small molecules in vivo, etc. It is hoped that the ideas and examples cited in this review article will further stimulate and optimize the full potential of coumarin based fluorescent probes, improve design selectivity, realize more simple and efficient applications in more fields, and help in the treatment of diseases

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