



Review

Organosilicon compounds as fluorescent chemosensors for fluoride anion recognition



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Contents

1. Introduction	25
2. Sensing F ⁻ based on high affinity between silicon and fluoride	25
2.1. F ⁻ triggered silicon–oxygen bond cleavage	25
2.1.1. BODIPY-based sensors	26
2.1.2. Coumarin-based sensors	27
2.1.3. BODIPY-coumarin based sensors	29
2.1.4. Fluorescein-based sensors	29
2.1.5. Naphthalimide-based sensors	31
2.1.6. Cyanine dye-based sensors	33
2.1.7. Thiazoles-based sensors	35
2.1.8. Quinoline-based sensors	36
2.1.9. Azo-based sensors	36
2.1.10. Pyrene-based sensors	37
2.1.11. Rhodamine-based sensors	37
2.1.12. Other fluorochrome-based sensors	38
2.1.13. F ⁻ triggered cyclization reaction	41
2.2. F ⁻ triggered silicon–carbon bond cleavage	43
2.2.1. BODIPY-based sensors	44
2.2.2. Pyrene-based sensors	44
2.2.3. Diketopyrrolopyrrole (DPP)-based sensors	44
2.2.4. Naphthalene–diimide-based sensors	45
2.2.5. Other systems	46
2.3. Sensors based on F–Si interactions	46
3. Conclusions and perspectives	47
Acknowledgments	49
References	49

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ABSTRACT

Recent developments in organosilicon-based chemosensors for F⁻ recognition are reviewed. The design strategies for improving the photophysical properties of organosilicon-based chemosensors are elaborated, with an emphasis placed on their utility for biological applications. The photophysical properties and electronic structures are analyzed in depth with reference made to the results of molecular modeling calculation and possible future research directions are assessed.

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1. Introduction

In recent years, there has been a strong focus on the development of recognition sensors for environmentally and biologically important anions [1–15], because of the vital role played by these anions in a wide range of chemical and biological processes [16–30,1,31–33]. The fluoride anion (F⁻) is one of the most significant in this regard due to its mild toxicity and important role in bone-growth and its presence in various environmental, clinical and food samples [34–38]. It is widely used as an additive in toothpastes and water to prevent dental caries and enamel demineralization resulting from wearing orthodontic appliances [39–43]. Fluorosis is caused by the elevated intake of fluoride over prolonged periods of time. An abnormal intake of a large dose or the chronic ingestion of lower doses of fluoride ions also produce ecological damage and cause dental or skeletal fluorosis, urolithiasis and nephrotoxic changes in humans, and even death [41,44–47]. To demonstrate the presence of fluoride in water at about 50 μM prevents tooth decay but at around 250 μM it causes mottled teeth and bone damage [48]. The United States Environmental Protection Agency (USEPA) mandates a drinking water standard for fluoride of 200 μM to prevent osteofluorosis and a secondary fluoride standard of 100 μM to protect against dental fluorosis [35].

Drinking water is the largest single contributor to daily fluoride intake [49]. Fluoride permeates naturally into the water supply due to solubilization of minerals that contain fluor, such as fluorapatite, cryolite and fluorite [50]. It is estimated that more than 100 million people regularly drink water which contains fluoride, of geogenic origin in concentrations that lie over the limit suggested by the World Health Organization guidelines [35]. Concerns have been raised about the manner in which the fluoride anion is introduced into the environment by anthropogenic activities, such as the use of phosphate containing fertilizers and by the aluminum processing industries. Different diseases are caused based on differing amounts of fluoride ingestion and the duration of intake. Dental fluorosis is caused by excessive fluoride levels and can cause white spots, yellowing of teeth and pitting or mottling of enamel. Skeletal fluorosis is a bone disease exclusively caused by excessive consumption of fluoride [51]. The detection and recognition of F⁻ has, therefore, become the focus of considerable research interest.

Until relatively recently, the methods that tended to be used for fluoride determination, such as fluoride-ion spectrophotometry [52,53], ion-selective electrodes [54,55], ¹⁹F NMR analysis [56], ion chromatography [57], reverse-phase HPLC [58] and fluorimetry [59,60], were broadly similar to those used for other inorganic ions. However, all these methods have significant disadvantages, such as complicated procedures, high expense, or their unsuitability for use in the field on environmental samples [61–63]. Recently, there has been a strong focus on the development of simple and effective fluorescent or colorimetric sensors for the

fluoride anion. Chemosensors enable the visual detection of the presence of fluoride anions and have been used for F⁻ recognition and detection based on noncovalent or covalent interactions with the sensor molecules, including hydrogen bonding between F⁻ and the NH protons of amides [64,65], indoles [66], pyrroles [67], urea and thiourea [68,69], Lewis acid coordination [70–72], and anion–π interactions [73,74]. This type of approach provides poor selectivity, however, because it is prone to interference by oxygen-containing basic anions, such as H₂PO₄⁻, CO₃²⁻ and AcO⁻, so these chemosensors can only be used in organic solvents to detect tetrabutylammonium (TBA⁺) fluoride and are not suitable for inorganic fluoride salts such as NaF [75–77].

Molecular recognition based on a specific chemical reaction provides higher selectivity and has attracted more attention from researchers in recent years. Over the last fifteen years, two different types of fluoride selective reaction-based detection strategies have been developed. Fluoride is a strong hydrogen-bond acceptor, and has a high affinity for silicon. Facile cleavage of either a C–Si or O–Si bond (bond-dissociation energies: 69 and 103 kcal/mol) by F⁻ has been the key to designing the reaction sites for these probes [78]. Various chemosensors have been reported based on these strategies. The aim of this review is to highlight and summarize the various approaches that have been used to design fluoride chemosensors based on organosilicons, the associated photophysical studies, and their biological applications since the year 2000. A critical assessment of research in the field is provided, which should inspire further research in the design of new organosilicon based chemosensors. This will form the basis for an overview of possible future directions in the analysis of environmental samples and in using chemosensors for biological imaging.

2. Sensing F⁻ based on high affinity between silicon and fluoride

2.1. F⁻ triggered silicon–oxygen bond cleavage

Silyl groups such as TMS (trimethylsilyl), TIPS (triisopropylsilyl), TBS (*tert*-butyldimethylsilyl), TBDPS (*tert*-butyldiphenylsilyl) are typically used to protect hydroxyl groups during organic synthesis. These protection groups render the corresponding dye inactive to interfering compounds, but there is easy cleavage upon attacking by F⁻. Upon reaction with F⁻, the protection group is removed to form an unprotected O⁻ anion. This results in significant differences in the electronic structure and hence also in the photophysical properties, including the UV–visible absorption spectra and the fluorescence quantum yield (Φ_F) values. As a result, numerous organosilicon compounds with Si–O bonds have been reported to act as chemosensors for the detection and recognition of F⁻. In this review, they are classified according to their organic fluorophore platforms into several different categories including

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