ABSTRACT

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TITLE: Design and Synthesis of Rhodamine based Fluorescent Molecular Probes for Iron (III) Recognition

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The rhodamine moiety is widely employed in designing fluorescent molecular sensors due to its fluorescence OFF-ON characteristics, which produce an intense fluorescence response upon interaction with specific guest molecule(s) that induces the opening of the Spiro lactam ring which is otherwise non-fluorescent in the Spiro lactam form..Iron is a crucial element involved in the proper functioning of various biological systems across all living organisms, including bacteria and plants. However, both iron deficiency and overload can lead to severe diseases such as Parkinson's, Huntington's, and Alzheimer's, among others. Given the significance of iron in biological processes and its role in disease, developing a chemosensor with high selectivity for Fe^{3+} that exhibits a fluorescence turn-on response is highly desirable for practical applications.

In this research endeavor, we have developed simple fluorescent molecular probes capable of selectively and sensitively detecting Fe^{3+} in a mixed organo-aqueous medium. Among them, a novel, highly sensitive, and selective fluorescent chemosensor, **RH-BZN (3)**, has been synthesized and thoroughly characterized. The sensor exhibits a strong preference for Fe^{3+}, forming a 1:1 complex in a 3:7 water:MeCN (v/v) mixture at pH 7.2. This interaction results in a remarkable 240-fold increase in fluorescence, with a binding constant (K_f) of $1.50\times10^{4}\ M^{-1}$. The fluorescence "turn-on" response is attributed to the opening of the spirolactam ring, which is otherwise non-fluorescent in its closed form. This interaction induces dual changes in absorbance and fluorescence, making **RH-BZN (3)** an efficient tool for Fe^{3+} detection.

Secondly, a novel and highly sensitive fluorescent chemosensor, **rhodamine-1-(2-aminoethyl)pyrrolidine** (L), has been synthesized and characterized using various physicochemical techniques. In a 3:7 water:MeCN (v/v) mixture at pH 7.2, this sensor exhibits exceptional selectivity for Fe^{3+} through 1:1 complexation, resulting in a remarkable 106-fold fluorescence enhancement with a binding constant (K_f) of $8.10\times10^{4}\ M^{-1}$. Fluorescence titration and anisotropy (r) studies were conducted in pure water in the presence of SDS. These studies revealed that the probe is likely trapped between two SDS monolayers, which interact via $\pi\ldots\pi$ stacking. This unique arrangement further influences the fluorescence intensity and anisotropy, as evidenced by the dependence on SDS concentration. Additionally, $[L\text{–}Fe]^{2+}$ thin films were fabricated on FTO glass substrates using the spin-coating deposition technique. The resulting film, with a thickness of $1.6\times10^{-5}\ cm^{1}$, was characterized for its optical properties, revealing a direct band gap (ε_g) of approximately 1.6 eV. These findings highlight the potential of **L** as a versatile sensor and functional material for practical applications.

The third chemosensor is a hexa-coordinated **N_2O** donor chelator that selectively detects Fe^{3+} both calorimetrically and fluorimetrically, with a remarkable 17-fold fluorescence enhancement in a 1:1 mixture of $CH_3CN\text{-}H_2O$ (v/v, pH 7.2, HEPES buffer). This fluorescence enhancement is attributed to the **chelation-enhanced fluorescence effect (CHEF)**, which arises due to the 1:1 complexation of the probe with Fe^{3+}, resulting in the formation of the **[L–Fe]** complex. Spectrophotometric and spectrofluorimetric titrations confirm the strong binding of the sensor to Fe^{3+}, with dissociation constants (K_d) of 6.26×10^{-5} M (UV-Vis) and 9.48×10^{-5} M (fluorescence titration). The detection limit of Fe^{3+} using **L** is 1.11 μM. **SEM (scanning electron microscope)** studies reveal interesting morphological changes in the microstructures: the probe **L** initially exhibits a block-like shape, which transforms into a spherical shape upon interaction with Fe^{3+}. Furthermore, when the **[L–Fe]** complex interacts with human serum albumin (HSA), an aggregated shape is observed. This probe (**L**) demonstrates great potential for on-site Fe^{3+} detection in the solid state, making it suitable for practical applications in sensing and monitoring Fe^{3+} ions.

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