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A Simple Phenothiazine Based Ratiometric Fluorescent Sensor for Hypochlorite Detection

*Disha Soni, Kajol Yadav, Raghu Chitta**
Department of Chemistry, School of Chemical Sciences and Pharmacy, Central University of Rajasthan, Bandarsindri, Tehsil: Kishangarh, Dist. Ajmer, Rajasthan-305817, India.
Email: raghuchitta@curaj.ac.in

Abstract:

Hypochlorite (ClO^-), an important reactive oxygen species (ROS), plays an important role in immune system. ClO^- is widely used as a disinfectant for treatment of water and other household purposes. Hence there is a need to develop highly sensitive and selective molecular probes for the detection of ClO^- in environmental and biological systems. Here, a simple phenothiazine based ratiometric fluorescent sensor **PTZ-Ph** for hypochlorite detection is presented. The detection limit of 0.36 μM was calculated. This probe was found to be selective for NaOCl as compared to other ROS, anions, and cations and also in presence of various interferents. Formation of sulfoxide was evident from the NMR titration experiment.

Key words: Ratiometric, fluorescent sensing, phenothiazine, hypochlorite, detection limit.

Introduction

There is a great need to develop sensors for various cations, anions, and ROS, which play an important role in biological systems and environment. Fluorescence is the most advantageous amongst various techniques due to its high sensitivity, relatively low costs, fast response time, and its easy implementation. Ratiometric sensing has an inherent benefit due to the emission intensity being monitored at two different wavelengths, which helps to eliminate the factors affecting the quantitative measurements like illumination intensity and optical path length. [1] Hypochlorite, when produced in excessive amounts in the body can cause tissue injury and many diseases. [2] Therefore, a ratiometric fluorescent sensor **PTZ-Ph** was synthesized and applied for selective and sensitive detection of hypochlorite.

Results and Discussion

All the sensing studies were carried out in MeOH:PBS buffer (2:3 v/v). The probe **PTZ-Ph** displayed the absorption peaks at 233, 264, and 314 nm. Upon addition of hypochlorite, the absorbance at 233 and 314 nm increased and a new peak at 285 nm was observed (Fig.1), which might be due to the oxidized product. The steady state fluorescence studies were performed to establish sensitivity and selectivity

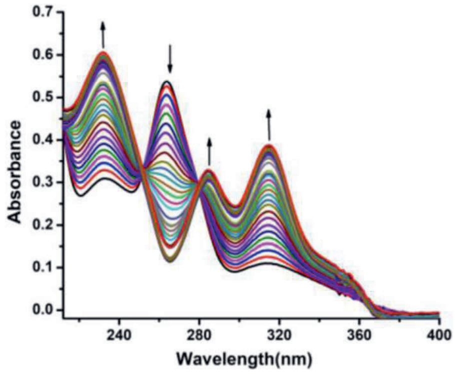

*Fig.1 Absorption titration spectra of **PTZ-Ph** (1.94×10^{-5} M) upon addition of NaOCl solution (2×10^{-3} M)*

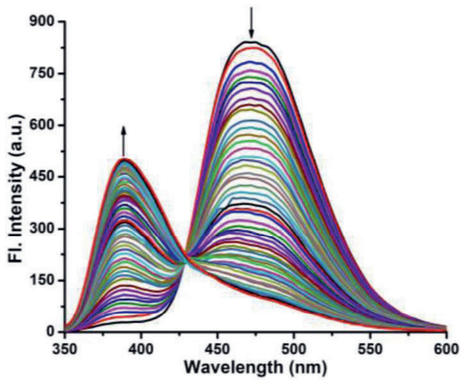

*Fig.2 Fluorescence spectra of **PTZ-Ph** (1×10^{-6} M) upon addition of NaOCl solution (4.7×10^{-5} M). λ_{ex}: 320 nm.*

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of the probe. The fluorescence spectra of **PTZ-Ph**, when excited at 320 nm showed a maximum peak at 473 nm but upon addition of incremental amounts of sodium hypochlorite solution, the emission at 473 nm started decreasing and a new peak at 388 nm started arising, depicting the ratiometric response of the probe (Fig.2). A calibration curve was plotted (Fig.3) and the detection limit was calculated to be 0.36 μM.

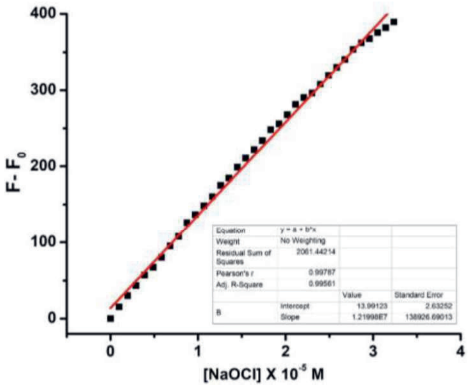

Fig. 3 Calibration curve for the detection limit calculation.

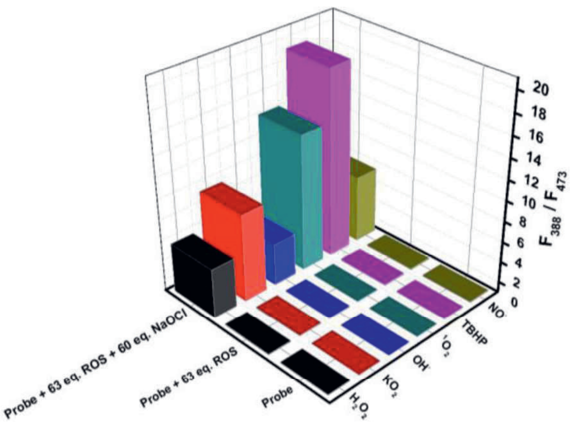

*Fig. 4 Bar graph depicting the effect of ROS on **PTZ-Ph** (1×10^{-6} M) probe and hypochlorite in presence of ROS (λ_{ex}: 320 nm).*

A time-dependent study was also performed with **PTZ-Ph** and NaOCl added, and it was found that the emission intensity was almost constant for 30 minutes.

To establish the selectivity of **PTZ-Ph** probe, the probe solution was treated with various ROS, anions, and cations. Only hypochlorite could induce the changes in the emission intensity. Next, competitive studies were also performed. The emission of probe on the addition of hypochlorite was monitored in presence of interferents and it was observed that hypochlorite could react with probe without being affected by any interferents (Fig. 4). This demonstrated the efficiency of probe **PTZ-Ph** for its application in complex biological and environmental systems.

To determine the species responsible for fluorescence enhancement, we synthesized the sulfoxide counterpart of the probe **PTZ-Ph-O** and recorded its NMR spectrum. NMR titration experiment was carried out by adding aliquots of NaOCl solution in **PTZ-Ph** in CD_3OD. It was observed that NMR of **PTZ-Ph-O** exactly matched with final titration spectrum, establishing sulfoxide as the major species being formed upon addition of NaOCl.

Conclusion

A ratiometric fluorescent probe **PTZ-Ph** was synthesized and used for hypochlorite detection. The detection limit was calculated to be 0.36 μM. NMR titration showed the formation of sulfoxide upon addition of NaOCl solution. It was also selective over other ROS, cations, and anions. NMR titrations showed the formation of sulfoxide as the major species. Computational, pH-dependent, and biological studies are in progress.

References

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