

DOCTORAL THESIS

Fluorescent chemosensor development based on multifunctional spirobenzopyrans

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Fluorescent Chemosensor Development Based on Multifunctional Spirobenzopyrans

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**A thesis submitted in partial fulfillment of the requirements for
the degree of
Doctor of Philosophy**

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Abstract

A number of spirobenzopyran-based optical sensors bearing different functionalized quinoline appendants were rationally designed and synthesized via efficient synthetic routes for the development of fluorescent Zn^{2+} chemosensors.

To lay down the foundation on novel design of Zn^{2+} sensory probes, sensor **SPAQ** constructed in facile via a convergent synthesis showed high selectivity and sensitivity towards Zn^{2+} albeit only in the medium of ethanol. Owing to the relative low binding constant ($K_a = 7.2 \times 10^4 \text{ M}^{-1}$) between the sensor and Zn^{2+} , the sensor failed in applying in aqueous solutions. A combined HRMS, 2D-NMR and NMR titration method was employed to establish the binding mode of the metal complex. Via a FRET mechanism between the 6-aminoquinoline and merocyanine moiety of **SPAQ**, upon binding with Zn^{2+} , ratiometric fluorescence outputs ($I_{645 \text{ nm}}/I_{470 \text{ nm}}$) were exploited for the quantification of the metal ion.

By changing the *O-N-N*-ligand of sensor **SPAQ** to *O-N-N-N*-ligand, as a simple avenue to improve the application scope of the sensor, sensor **SPQN** exhibited highly selective and sensitive fluorescent response towards Zn^{2+} in aqueous solutions. In addition to being a selective fluorescent Zn^{2+} chemosensor, **SPQN** can serve as a naked-eye detecting agent for Zn^{2+} as the metal recognition process is characterized by the formation of red color from a colorless sensor solution. Fluorescence titrations of the sensor with a variety of divalent cations revealed that a

much higher binding constant ($K_a = 7.26 \times 10^6 \text{ M}^{-1}$) was found for the complex of **SPQN** and Zn^{2+} in comparison with its counterparts deriving from alkali earth metal and other transition metal ions. The binding mode of the sensor and Zn^{2+} metal was manifested by fluorescent Job's plot, HRMS and 2D-NMR spectroscopic method. A clear FRET phenomenon between the two fluorochromic moieties of **SPQN** allowed the development of the sensor as a ratiometric probe. Furthermore, the rich spectroscopic properties of **SPQN** in interacting with metal ions provide a platform for the development of an **OR** and **INHIBIT** logic gate.

To continue the innovation of Zn^{2+} sensing targeted with NIR emissive outputs operative in aqueous solutions, **SPQH** was designed and synthesized and the conjugated system of spirobenzopyran was elongated through the formation of C=N bond. The appendage of multi-functional receptive groups onto the spirobenzopyran scaffold in **SPQH** furnishes the fluorescent metal chelator with at least four metal coordinating sites, enabling the formation of a tight complex with Zn^{2+} . Thus, the ratiometric detection of Zn^{2+} in physiological condition with a NIR emission and an extremely high binding constant ($K_a = 1.37 \times 10^7 \text{ M}^{-1}$) was achieved.

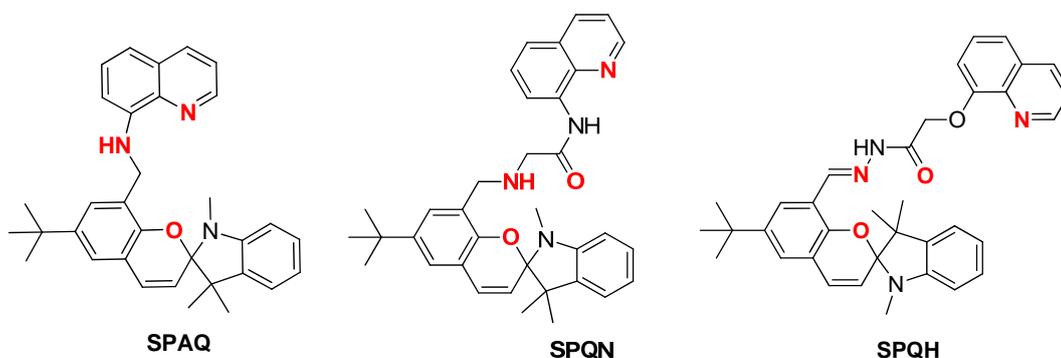


Table of contents

Declaration	i
Abstract	ii
Acknowledgements	iv
Table of contents	v
List of Figures	viii
List of Schemes	xiii
List of Tables	xiv
Chapter 1 Introduction	1
1.1 Supramolecular Chemistry	1
1.2 Fluorescent Chemosensor for Ion Recognition	2
1.3 Common Signal Transduction Mechanisms of Fluorescent Sensors.....	3
1.4 Spirobenzopyran (SP) - a Molecular Scaffold Integrating Binding Unit as well as Signaling Unit.....	9
1.5 References	16
Chapter 2 Ratio-metric Zn²⁺ Sensing in Organic Solvent Based on a Spirobenzopyran and Quinoline Dyad	20
2.1 Introduction	20
2.2 Design and Synthesis of Zn ²⁺ Sensor SPAQ via FRET Mechanism.....	21
2.3 Analytical Characterization of Sensor SPAQ for Zn ²⁺	24

2.4 Fluorescent Signal Transduction Process Study of SPAQ for Zn^{2+}	27
2.5 Binding Mode Study of SPAQ and Zn^{2+}	31
2.6 Experimental Section.....	37
2.7 Summary.....	39
2.8 References and Notes	40
Chapter 3 A Colorimetric and Fluorescent Turn-on Chemosensor	
Operative in Aqueous Media for Zn^{2+} Based on a	
Multifunctionalized Spirobenzopyran Derivative	
	43
3.1 Introduction	43
3.2 Design and Synthesis of Zn^{2+} Sensor SPQN	44
3.3 Analytical Characterization of Sensor SPQN towards Metal Ions.....	46
3.4 Fluorescent Signal Transduction Process Study of SPQN for Zn^{2+}	55
3.5 Binding Model Study of SPQN and Zn^{2+}	59
3.6 Logic Gate	62
3.7 Experimental Section.....	64
3.8 Summary.....	68
3.9 Notes and References	69
Chapter 4 A Near Infrared (NIR) Ratiometric Fluorescent Sensor	
for Zn^{2+} Based on Spirobenzopyran Platform.....	
	70
4.1 Introduction	71
4.2 Design and Synthesis of Zn^{2+} Sensor SPQH	73

4.3 Analytical Characterization of Sensor SPQH for Zn^{2+}	74
4.4 Binding Mode Study of SPQH and Zn^{2+}	79
4.5 Experimental Section.....	83
4.6 Summary.....	86
4.7 References and Notes	86
Chapter 5 Summary and Future Work	89
Appendices	93
Curriculum Vitae	123