DOCTORAL THESIS

Fluorescent chemosensor development based on multifunctional spirobenzopyrans

Zhu, Jianfa

Date of Award:
2011

Fluorescent Chemosensor Development Based on Multifunctional Spirobenzopyrans

ZHU Jianfa

A thesis submitted in partial fulfillment of the requirements for the degree of

Doctor of Philosophy

Principal Supervisor: Professor CHAN Wing Hong

Hong Kong Baptist University

June 2011

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 x 10^4 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 ($I_{645\ nm}/I_{470\ nm}$) 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 x 10^6 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 x 10^7 M^{-1}) was achieved.

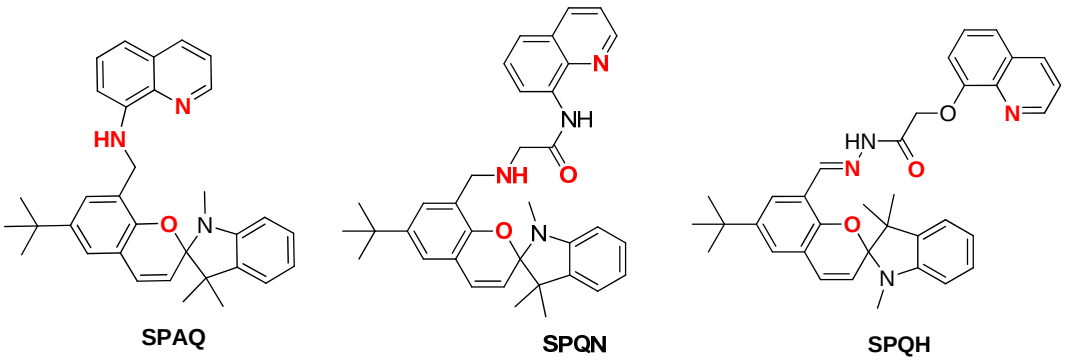

Table of contents