MASTER'S THESIS

Development of optical chemosensors for cation sensing

Cheung, Sin Man

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Development of Optical Chemosensors for Cation Sensing

CHEUNG Sin Man

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Principal Supervisor: Prof. CHAN Wing Hong

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Abstract

Novel fluorescent chemosensors **FS1**, **FS2** and **FS3** based on the "fluorophore-spacer-receptor" design have been developed for chemosensing of mercury ion. Starting from aniline, they were synthesized in a sequence of five high yield reactions. **FS1** and **FS2** contain an anthracene group as the fluorescent signaling subunit and two cooperative dithiocarbamate moieties as the metal receptor. The host guest interaction between the chemosensors and transition metal ions were investigated by using fluorescence measurements.

50% aqueous ethanol solution was used as the solvent system for the fluorescent titration experiments. Both **FS1** and **FS2** showed a local excited state emission (LE) and an intramolecular charge transfer state emission (ICT). When binding with Hg^{2+}, the LE of **FS1** increased at 425 nm and the ICT decreased at 467 nm; while the ICT of **FS2** decreased at 500 nm leaving the LC at 417 nm remained unchanged. The detection limit of two sensors could reach to 10^{-8} M, but the selectivity of **FS2** toward common metal ions was much better than that of **FS1**. **FS2** only chelated with Hg^{2+} and Ag^{+} and there was no significant responds toward other potentially interfering ions. **FS2** was also proved to be pH-independent that could be function as a chemosensor in an unbuffered solution.

To confirm the receptive nature of the dithiocarbamate groups, **FS3** lacking of the ligating functionalities was synthesized as an analog. After coordinating metal ions, it did not give an ICT emission. Instead, only an enhancement of the LE fluorescence at

415 nm, as a result of PET effect was observable.

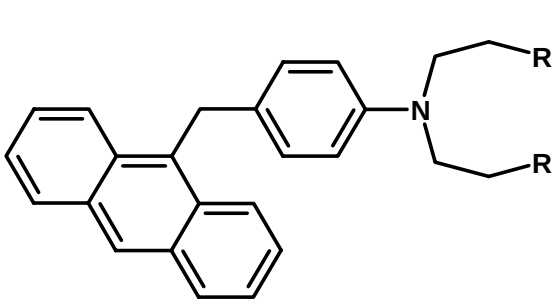
Four chromogenic chemosensors **SP1**, **SP2**, **SP3** and **SP4** bearing spirobenzopyran skeleton were synthesized in a four-step synthetic route. The photostability of the compounds was much enhanced by incorporating a *tert*-butyl group on the C-6' position while their chelating ability was conferred by the aminomethyl group appended on the C-8' position. The photochromic behaviors of the sensors toward Cu^{2+} were investigated by absorption and fluorescence spectroscopies.

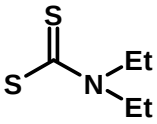
SP1 was developed as a potential Cu^{2+} selective fluorescent sensor based on the inner filter effect. It can also recognize and quantify cysteine and homocysteine in neutral aqueous solution.

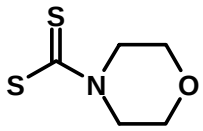
SP2 was found to be selectively coordinated with Cu^{2+} in aqueous ethanolic solution (i.e. EtOH:H_2O = 6:4). When sequential amount of Cu^{2+} solution was added to the sensor solution, the colorless **SP2** solution turned to red and three increasing absorption peaks at 382, 450, 536 nm were recorded.

SP4 was also found to be highly selective to Cu^{2+} in absolute EtOH. When Cu^{2+} was added into **SP4** solutions, a purple color was observed. It gave two increasing absorption peaks at 384 and 533 nm and a decreasing peak at 233 nm in response to this metal ion stimulus. An isosbestic point appeared at 256 nm in the spectrum for the titration with Cu^{2+}. The coordination stoichiometry of **SP4** with Cu^{2+} was found to be 1:1. When excited at 270 nm, a fluorescent emission at 355 nm decreased in such that a quench ratio of 58% was recorded. The limit of detection was estimated to about 5 X

10^{-8} M. The switching cycle comprising **SP4**, **ME** and **MEH** state was also established by the use of sequential Cu^{2+}, acid and base stimuli.



FS1, R= 

FS2, R= 

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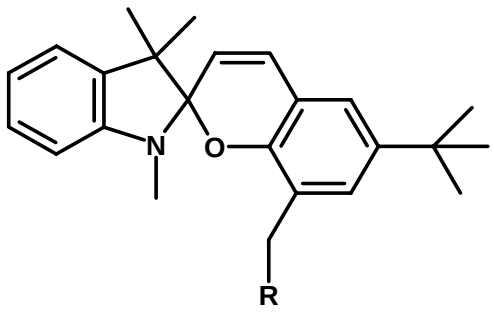

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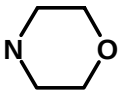
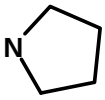
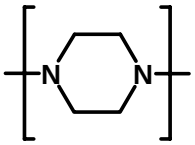
SP2, R= 

SP3, R= 

SP4, R= 

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