

## Sulfoxides as response elements for fluorescent chemosensors: Does it work?

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Received 2 December 2014; Accepted (in revised version) 31 January 2015

Published Online 1 March 2015

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**Abstract.** Our density functional theory (DFT)/time-dependent DFT (TDDFT) calculations for the sensing mechanism of a series of sulfoxide based metal-responsive fluorescent chemosensors, suggested that the intramolecular charge transfer (ICT) is not a reasonable mechanism for these chemosensors. The calculated electronic transition energies, the corresponding oscillator strengths of these chemosensors and the involving frontier molecular orbital analysis indicated that there is no obviously ICT state with a transition oscillator strength approaching to zero. The fluorescence quenching of these chemosensors cannot be explained by ICT process. The ground state optimized structures of chemosensors and their complexes indicated that there might be twisted excited configuration for these chemosensors and the twisted excited state configuration may response for the fluorescence quenching. The configuration change can be blocked in the Zn complex that is responsible for these complexes showing fluorescence emission enhancement. In order to understand the function of the sulfoxides group in these metal-responsive fluorescent chemosensors, excited state configuration optimization as well as the excited state hydrogen bond effect on the fluorescence enhancement in the aqueous solvent will be conducted.

**PACS:** 34.70.+e; 42.70.-a

**Key words:** Fluorescent probes; Sensing mechanism; Density functional calculations; Intramolecular charge transfer (ICT); sulfoxide moiety.

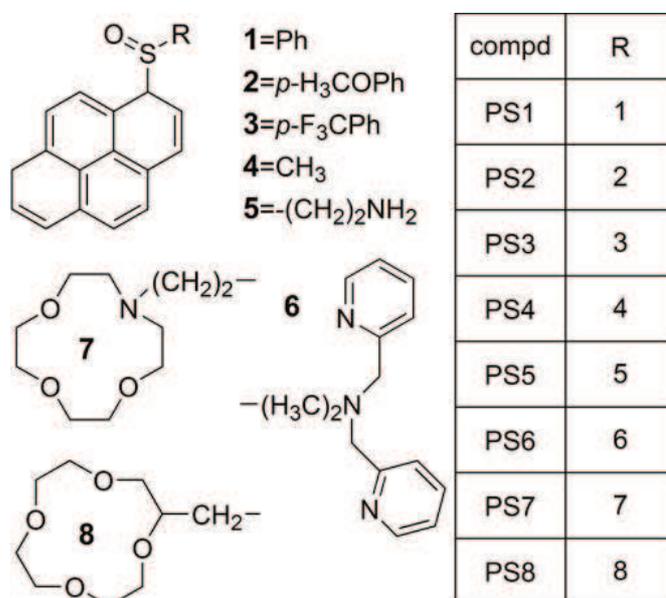
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## 1 Introduction

Metal ions play important roles in fundamental life processes, such as catalysis, metabolism, biomineralization, osmotic regulation, signaling and so on [1]. Heavy metal ions pollution is a serious problem in some districts of the world. The released heavy metal ions from industrial waste have already polluted the water sources (groundwater, lakes, streams and rivers) in some part of the world. Hence quantitatively metal ions detection is important for understanding life processes, human health and environmental protections [1-2]. Fluorescent chemosensor for metal ion detection has attracted broad attention due to its easy operation, low cost and high sensitivity [1-2]. A large number of fluorescent chemosensors have a good performance for detecting metal ions have been reported [1-3]. Most of reported organic fluorescent chemosensors, which are based on coordination interaction between metal ions, contain nitrogen atoms which act as coordination binding atoms for metal ions [1-4]. This sort of fluorescent chemosensors are acid sensitivity and depend on the fluorescence response on nitrogen coordination chemistry [4]. These limitations can influence the performance of the fluorescent chemosensors for detecting metal ions.

Recently, Kathayat and coworker developed series of metal-responsive fluorescent chemosensors (as shown in Scheme 1, PS1-PS8) by utilizing sulfoxides as reporting functional groups [4]. These sulfoxide based fluorescent chemosensors PS1-PS8 show low fluorescence quantum yield [4]. They proposed that the fluorescence quenching phenomenon is ascribed to intramolecular charge transfer (ICT) from the sulfoxide to the



Scheme. 1: Structures of compounds PS1-PS8.