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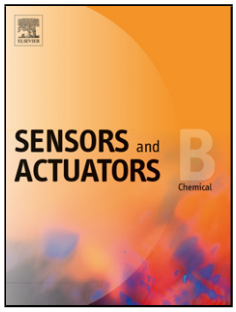

Title: “Turn off-on” phosphorescent sensor for biothiols based on a Ru-Cu ensemble

Authors: Pingyu Zhang, Yi Wang, Wenxiu Huang, Zhiqian Zhao, Haihang Li, Haitao Wang, Chuanxin He, Jianhong Liu, Qianling Zhang

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<AT>``Turn off-on" phosphorescent sensor for biothiols based on a Ru-Cu ensemble

<AU>Pingyu Zhang, Yi Wang, Wenxiu Huang, Zhiqian Zhao, Haihang Li, Haitao Wang, Chuanxin He*, Jianhong Liu and Qianling Zhang* ##Email##zhql@szu.edu.cn##/Email##
<AU>
<AFF>Shenzhen Key Laboratory of Functional Polymer, College of Chemistry and Environmental Engineering, Shenzhen University, Shenzhen, Guangdong 518060, PR China

Author information

<ABS-HEAD>Highlights► Construct a novel non-phosphorescent Ru-Cu ensemble ► Turn off-on phosphorescence with high selectivity and insensitivity ► Biothiols sensor in living cancer cells

<ABS-HEAD>ABSTRACT
<ABS-P>Glutathione (GSH), cysteine (Cys), and homocysteine (Hcy) are three major biothiols, which play key roles in various biological systems. Accordingly, the development of phosphorescent probe of biothiols has attracted great attention in clinical applications. Here we report a ruthenium polypyridyl complex (**1**), which shows large phosphorescence quenching with 2.0 equivalents of Cu^{2+} ions. The non-phosphorescent **1**−Cu ensemble sensor is formed and further applied to detect biothiols in living cancer cells. Among the various amino acids, GSH, Cys and Hcy induce distinct turn-on phosphorescence with high selectivity and insensitivity to biological relevant pH range and other proteins. As we know, this is the first report that Ru−Cu ensemble is used for probing endogenous thiols in the living cells.
<KWD>Keywords: Ru-Cu ensemble; Phosphorescent sensor; Biothiols; Turn off-on

<H1>1. Introduction

Cysteine (Cys), homocysteine (Hcy), and glutathione (GSH) are major biothiols which play a central role in maintaining biological homeostasis in living cells [1-6]. Deficiencies in Cys can lead to many aberrations, such as hematopoiesis decreases, leucocyte loss, and psoriasis, among others [7,8]. High concentrations of Hcy are involved in cardiovascular and coronary heart diseases [9]. GSH is involved in controlling the redox environment in cells and deficiency accompanies many diseases such as cancer [10,11]. Therefore, it is of great importance to develop methods for effectively and selectively detection of biothiols.

In the past few years, considerable efforts have been made to develop luminescent probes for these biothiols. Even though many fluorescent biothiol probes have been reported before, most of them are reaction based chemical sensors [12-17]. Another promising approach is to design biothiol selective fluorescent ensembles [18-21]. In this approach, researchers take advantage of the fluorescence quenching properties of transition metal ions/nanoparticles by either energy or electrons transfer to the partially filled the orbitals of the metal ions/nanoparticles. Accordingly, non-fluorescent copper ensembles and their thiol-facilitated fluorescence enhancements have been considered as one of the key approaches.

The utilization of luminescent transition metal complexes for various applications has witnessed tremendous growth over the past several decades, particularly as luminescent imaging [22,23], for protein biomarkers [24], or for luminescent sensor [25,26]. Transition metal complexes have several useful qualities for these applications. Their ligands can be varied in order to tune their photophysical properties and interactions with

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