

Abstract

This thesis entitled "*New approaches for the development of chromo-fluorogenic sensors for chemical species of biological, industrial and environmental interest*" is focused on the development of new chromo-fluorogenic chemosensors based on the basic principles of supramolecular chemistry; particularly in molecular recognition and self-assembly.

The first stage of this work consisted on an extensive and thorough literature exploration that led to the publication of a review article about chromogenic and fluorogenic chemosensors for anions recognition that were published during the years 2010 and 2011 (Santos-Figueroa, LE, et al. *Chem Soc Rev.*, **2013**, 42, 3489-3613). This literature review, although not has been explicitly included in this PhD thesis, due to its long stretch, is without a doubt a part of the theoretical basis of the experimental work exposed here, thus it is continually cited as reference.

This PhD thesis is structured in four chapters. The first is a general introduction that summarizes the theoretical foundations of supramolecular chemistry in which the practical studies are based. In the next three chapters, the main results of the experimental phase of this thesis are condensed. The order in which they are shown follow a logical scheme that promotes a better understanding and it not represent timing of when they were made.

Chapter 2 is devoted to the synthesis, characterization and coordination studies with metal cations of a chromo-fluorogenic receptor constructed by binding site-signaling subunit approach. The synthetic receptor employs a chalcone skeleton as signaling subunit and it is functionalized with two groups that make up an electron donor-acceptor system, forming a molecule, which have a charge transfer band in the visible spectrum region. Of all cations and anions tested, only the trivalent (Fe^{3+} , Al^{3+} and Cr^{3+}) are able to induce significant changes in the absorption bands of the visible zone and in the emission. The receptor allows screening of trivalent cations with remarkable limits of detection in the 2-4 nM range of concentrations and optical changes noticeable to the naked eye (*Chem Eur J.*, **2014**, submitted).

Moreover, chapter three is devoted to the synthesis, characterization and anion coordination studies of chromo-fluorogenic chemosensors constructed by binding site-signaling subunit approach, displacement assays and chemodosimeter. By binding site-signaling subunit approach, seven thiosemicarbazones-based receptors have been prepared with furan ring functionalized with two electron donor and acceptor groups in order to modulate the selectivity in coordination towards anions. In the presence of basic anions (fluoride, cyanide, acetate and dihydrogen phosphate) significant color and emission changes has been associated to coordination and deprotonation processes into the receptors (*Org. Biomol. Chem*, **2012**, 10, 7418-7428). Other four thiosemicarbazones-based probes synthesized

using thiophene rings, also showed significant fluorescence and color changes in the presence of the same basic anions (*Tetrahedron*, **2012**, 68, 7179-7186). The displacement assays approach have been used to develop a selective fluorimetric sensor for hydrogen sulfide anion in aqueous environments and cell media. With this goal, we have prepared a non-fluorescent cyclam-Cu(II) complex with anthracene moiety. In this case, hydrogen sulfide anion is capable of displacing the Cu(II) from cyclam ring, this causes a switch on in the fluorescence of the system with a gradual increase in emission intensity as a function of the amount of analyte detected (*Eur. J. Inorg. Chem*, **2014**, 41-45). Subsequently, the approach of the chemodosimeter was used to prepare a chromo-fluorogenic probe for detection of hydrogen sulfide in aqueous solutions. In this case, an azo dye functionalized with a sulfonyl azide group was synthesized. In the presence of hydrogen sulfide a reduction from sulfonyl azide to sulfonyl amide taking place with a noticeable color change with the naked eye and an enhancement fluorescence intensity (*Eur. J. Org. Chem*, **2014**, 1848-1854).

Finally, Chapter 4 of this thesis shown the development of a sensor hybrid material for sulfite anion recognition in aqueous media. For it, a stilbene skeleton-base chemodosimeter has been encapsulated within the hydrophobic pockets of mesoporous silica nanoparticles. Upon addition of the sulfite anion to aqueous nanoparticles suspensions, a significant increase in fluorescence due to the reaction between the anion and the chemodosimeter within the cavities of the support is observed. Additionally, a functional system with the use of the hybrid material prepared and a monolith as polymeric support were employed for testing detection of sulfite in commercial wine (*Angew. Chem Int Ed*, **2013**, 52, 13712-13716).

For all the above we can say that this PhD thesis constitutes an original scientific contribution to the development of molecular and supramolecular chemistry. Its content and publications derived from the studies presented in the thesis leaves open routes to continue the study and development of new and more efficient chemical sensors and hybrid detection systems with biological, industrial and environmental applications.