

Abstract

The present PhD thesis entitled “Molecular probes and ruthenium (II) and osmium (II) complexes for the chromo-fluorogenic sensing of charged species and carbon monoxide” is focused on the development of molecular chemosensors. More in detail, the work carried out is clearly divided into two independent parts: (i) the synthesis and characterization of multifunctional molecular probes for the optical detection of anions and metal cations and, (ii) the preparation of ruthenium (II) and osmium (II) complexes for the chromo-fluorogenic sensing of carbon monoxide.

The first family of molecular probes, reported in chapter 2, is based on the use of imidazoanthraquinone as signaling subunit. Using this molecular fragment four probes (**2a-2d**) are prepared and characterized. Of all the anions tested, only fluoride is able to induce the appearance of red-shifted absorption (reflected in marked color changes) and emission bands. These changes are ascribed to a fluoride-induced deprotonation of the N-H moiety of the imidazole ring. Also Fe^{3+} , Al^{3+} and Cr^{3+} were able to induce moderate blue-shifts of the absorption bands of the four receptors upon coordination (with the oxygen and nitrogen atoms of the imidazoanthraquinone chromophore) and marked emission quenching.

The second chapter is also devoted to study the coordination behavior toward anions and cations of a second family of probes (**3a-3d**) containing imidazoquinoline derivatives. Again, fluoride anion promoted the deprotonation on the probes that are reflected in the appearance of red-shifted absorption and emission bands. The optical response in the presence of metal cations is quite unselective and UV-visible shifts and emission quenchings are observed in the presence of Hg^{2+} , Cu^{2+} , Co^{2+} , Fe^{3+} , Fe^{2+} , Zn^{2+} , Pb^{2+} , Cd^{2+} , Cr^{3+} and Al^{3+} .

Chapter 3 presents the synthesis, characterization and chromo-fluorogenic behavior toward of carbon monoxide of two set of ruthenium (II) and osmium (II) complexes bearing 2,1,3-benzothiadiazole (BTD) and 5-(3-thienyl)-2,1,3-benzothiadiazole (TBTD) fluorophores. Eight complexes functionalized with BTD ligand (**1-8**) are prepared in the first part of this chapter. Chloroform solutions of the complexes underwent remarkable color changes when CO is bubbled. Also, significative emission enhancements are observed due to coordination of CO and displacement of BTD fluorophore. Besides, the adsorption of the complexes on silica yielded solids that presented remarkable color changes that allowed a naked eye detection of CO in gas phase.

The second set of ruthenium (II) and osmium (II) complexes contains TBTD fluorophore (**3-7**). Also these complexes are able to detect CO in chloroform solution and in gas phase when adsorbed on silica through color and fluorescence changes. Moreover, two new complexes (**8** and **9**) containing a poly(ethylene) glycol chain are prepared. Both complexes are water soluble

and allowed CO detection in this highly competitive solvent. Besides, **8** and **9** are non-toxic and are successfully used for CO detection in HeLa cells.