

ABSTRACT

The work done in this thesis can be divided into three sections that correspond to the synthesis and study of several families of sensors for the detection of cations and anions:

First, it has carried out the synthesis and characterization of a family of ligands containing different cation binding sites covalently connected to a thiopyrylium signalling reporter. The receptors L^1-L^6 are able to signal the presence of certain metal cations *via* three different channels; electrochemically, fluorogenically and chromogenically. An acetonitrile solution of L^1-L^6 shows a bright blue colour due to a charge-transfer band in the 575–585 nm region. The colour variation in acetonitrile of L^1-L^6 in the presence of the metal cations Ag^+ , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+} has been studied. A selective hypsochromic shift of the blue band was found for the systems L^4-Pb^{2+} and L^5-Hg^{2+} . Additionally, L^1-L^6 are poorly fluorescent but coordination with certain metal cations induces an enhancement of the fluorescence at ca 500 nm. For instance, the presence of Cu^{2+} and Fe^{3+} induced a remarkable 42-fold and 45-fold enhancement in the emission intensity of L^1 centred at 500 nm, respectively. Also remarkable was the 18-fold enhancement observed for L^4 and L^5 in the presence of Fe^{3+} and Cu^{2+} , respectively. The electrochemical behaviour of receptors L^1-L^6 was studied in acetonitrile using platinum as a working electrode and $[Bu_4N][BF_4]$ as a supporting electrolyte. This family of receptors showed a one-electron reversible redox process at ca. -0.46 V *versus* sce attributed to the reduction of the thiopyrylium group. A moderate anodic shift in the presence of certain metal cations was observed. The effect in the UV-visible spectra of acetonitrile solutions of receptor L^1-L^6 in the presence of anions was also studied. A remarkable bleaching was found in the presence of cyanide.

In the same line of action, has synthesized a new sensor (L^7) for colorimetric detection of cyanide by electrophilic aromatic substitution between N, N-dioctylanilina with 2,6- difenilpirilio perchlorate in anhydrous DMF, followed by the replacement of oxygen atom in the pyrylium ring by a sulphur atom with Na_2S . The basis of the detection lies in the nucleophilic addition of cyanide anion to the central aromatic thiopirilio ring. The results obtained in organic solution, showed a selective response to cyanide anions over F^- , Cl^- , Br^- , I^- , AcO^- , NO_3^- , NCS^- , $H_2PO_4^-$ and HSO_4^- . For use in aqueous media thought encapsulated in micelles by using a surfactant. In order to overcome the competition of the anion OH^- in the mechanism of attack, and at same time a pH at which exist the CN^- nucleophilic species, we selected a pH of 9.5 (at lower pH protonation occurs giving cyanide HCN). Spectroscopic studies of the sensor system / surfactant in water, show a sensitive and selective detection of cyanide over other anions. By adding cyanide sensor solutions / surfactant is a loss of intensity of the visible band centered at 575 nm. This progressive loss of colour is assigned to a nucleophilic attack of cyanide anion on certain carbon atoms of the heterocycle tiopirilio. This attack breaks the conjugation of the system produces a loss of colour. Furthermore, studies have been conducted NMR- H^1 to check on that ring carbons occurs tiopirilio attack. It notes that the cyanide anion is added to the carbons C2 and C4 by 75% to 25%.

Second, we have studied the UV-visible behaviour of a new family of phenyl-thiosemicarbazone dyes (L^8-L^{16})

linked to different furan, thiazole, (bi)thiophene and arylthiophene π -conjugated bridges were synthesized in good yields and their response toward anions was studied. Acetonitrile solutions of L^8 - L^{16} show bands in the 326-407 nm region that are modulated by the electron donor or acceptor strength of the groups appended to the phenyl-thiosemicarbazone moiety. Anions of different shape such as F^- , Cl^- , Br^- , I^- , ACO^- , NO_3^- , NCS^- , CN^- , $H_2PO_4^-$ and HSO_4^- were employed for the recognition studies. From these anions, only fluoride, cyanide, acetate and dihydrogen phosphate displayed sensing features. Two different effects were observed, (i) a low bathochromic shift of the absorption band due to coordination of the anions with the thiourea protons and (ii) the growth of a new red shifted band with a concomitant change of the solution from yellow or pale yellow to orange-red due to deprotonation. The extent of each process is a balance between the acidity tendency of the thioureido-NH donors modulated by the donor or acceptor groups in the structure of the receptors and the basicity of the anions. Fluorescence studies were also in agreement with the different effects observed on the UV/Vis titrations. Stability constants for the two processes (complex formation + deprotonation) for selected receptors and the anions fluoride and acetate were determined spectrophotometrically using the program HYPERQUAD. Semiempirical calculations to evaluate the hydrogen-donating ability of the dyes and 1H NMR titrations experiments with fluoride were carried out. A prospective electrochemical characterization of compound L^{10} in the presence of anions was also performed.

Finally, we proceeded to the synthesis, characterization and study of the response to metal cations (Ag^+ , Cd^{2+} , Cu^{2+} , Fe^{3+} , Hg^{2+} , Ni^{2+} , Pb^{2+} and Zn^{2+}) from a family of receptors chromogenic functionalized crown ethers and azo-thiazole derivatives dyes (L^{17} - L^{22}). An acetonitrile solution of L^{17} - L^{22} shows a bright blue colour due to a charge-transfer band centred in 580 nm. The selective coordination of some metal cations with macrocyclic unit receptors produces significant move of the band of the visible. The responses showed more selective the L^{20} and L^{21} receivers with Pb^{2+} and Hg^{2+} , respectively. The presence of these two cations induces large shifts to the blue of the charge transfer band. These shifts toward the blue are indicative of a preferential coordination to the macrocycle. The most interesting result is obtained with L^{21} . Thus, charge transfer band L^{21} receptor undergoes a displacement of 180 nm in the presence of Hg^{2+} .