NOVEL BENZIMIDAZO[1,2-*a*]QUINOLINES AS pH SENSORS AND CHEMOSENSORS

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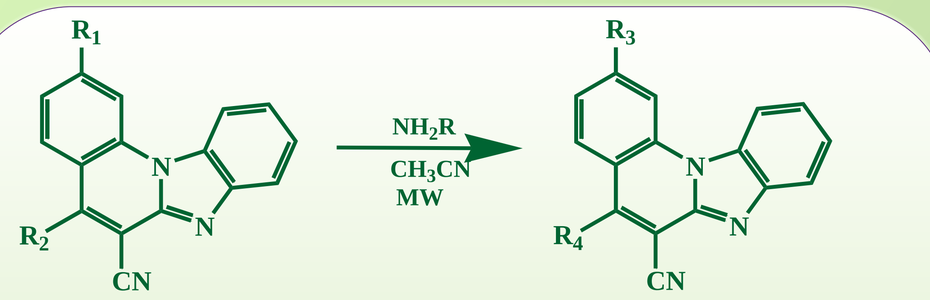
INTRODUCTION

In recent years there is a permanent and growing interest in the synthesis of benzannulated benzmidazole derivatives, as a one of the most important groups of nitrogen heterocycles, as a direct consequence of their great importance in the natural, medicinal and environmental sciences. Cyclic benzimidazole derivatives due to excellent spectroscopic properties are important for their application in optoelectronics or as chemosensors, with side chain substituents designed to enable interactions with potential biological targets.

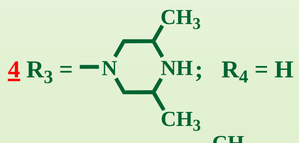
SYNTHESIS

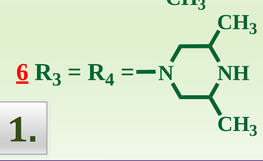
For the synthesis of benzimidazo[1,2-*a*]quinolines, classical and microwave assisted reactions were used.



1 $R_1 = F; R_2 = H$
2 $R_1 = F; R_2 = Cl$

3 $R_3 = NHCH_2CH_2CH(CH_3)_2; R_4 = H$
5 $R_3 = R_4 = NHCH_2CH_2CH(CH_3)_2$

4 $R_3 =$  $R_4 = H$

6 $R_3 = R_4 =$ 

Scheme 1.

SPECTROSCOPIC CHARACTERIZATION

Due to the highly conjugated planar tetracyclic chromophore, prepared compounds showed interesting spectroscopic properties which were studied by using UV/Vis and fluorescence spectroscopy in several solvents.

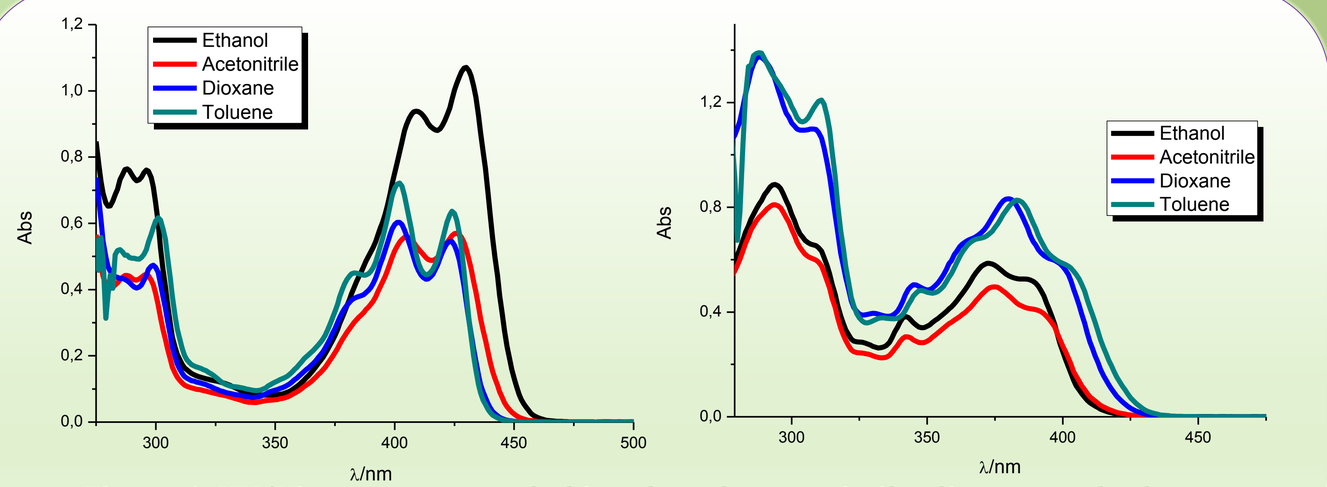


Figure 1. UV/Vis spectra recorded in ethanol, acetonitrile, dioxane and toluene at concentration of 2×10^{-5} moldm^{-3} of compounds 3 and 5

In addition, to prove their possible analytical applications for the detection of cations in solutions as well as pH sensors, their spectroscopic properties were studied in the presence of different metal cations and depending on different pH of used solution.

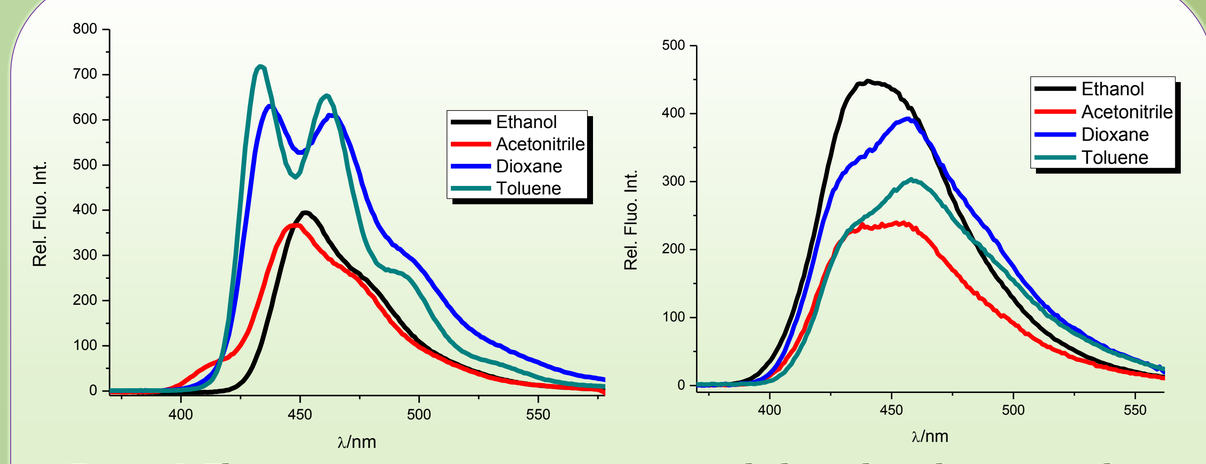


Figure 2. Fluorescence emission spectra recorded in ethanol, acetonitrile, dioxane and toluene at concentration of 1×10^{-7} moldm^{-3} of compounds 3 and 5

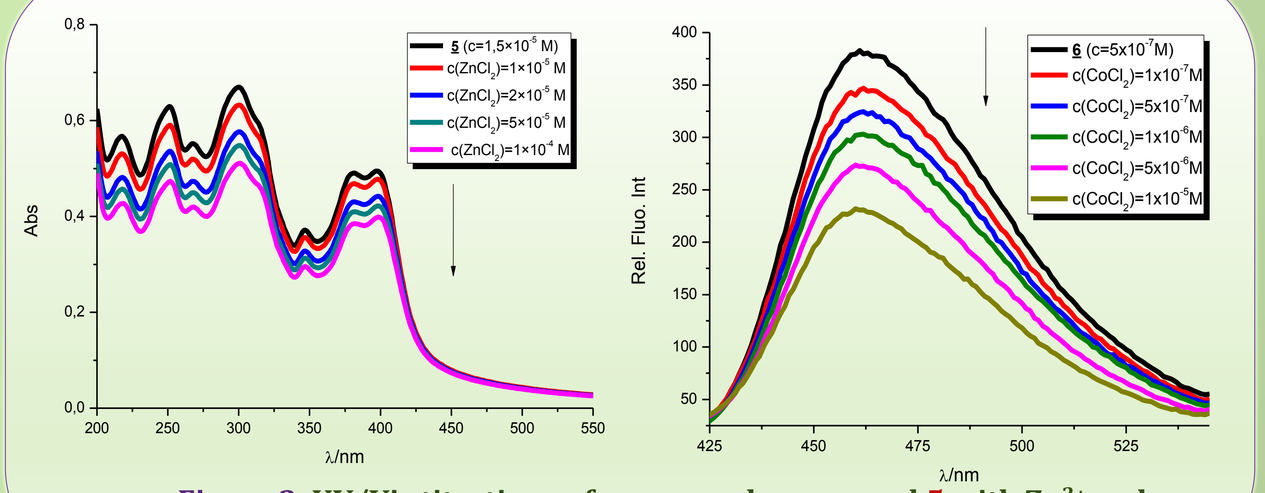


Figure 3. UV/Vis titrations of compound compound 5 with Zn^{2+} and fluorimetric titrations of compound 6 with Co^{2+}

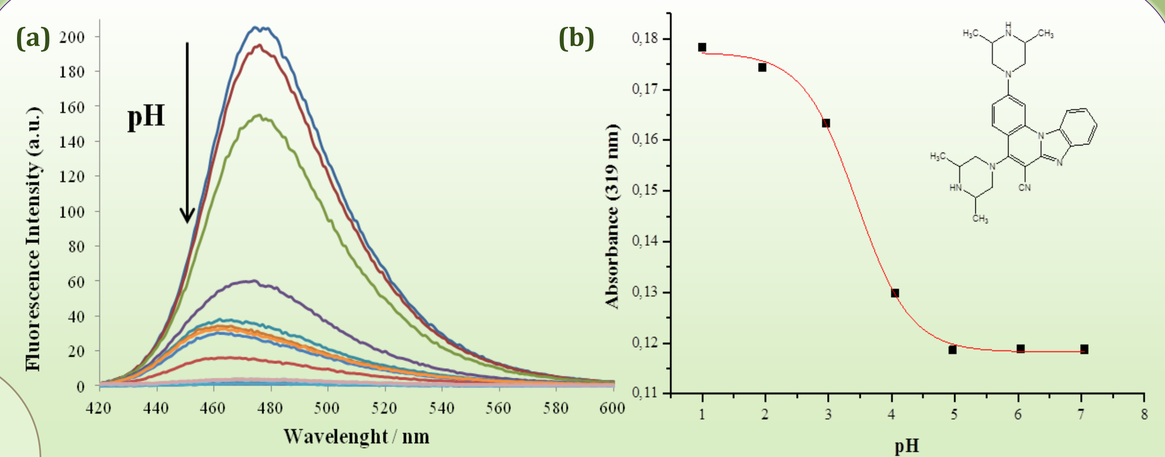


Figure 4 (a) Fluorescence emission spectra of compound 6, 2 x 10^{-6} mol dm^{-3} in aqueous solutions at different pH values; (b) Calibration curve of chromophore 6; absorbance versus pH at 319 nm

Compound 3 showed interested selectivity toward Zn^{2+} cation which could offer the possibility for its application for imaging and quantification Zn^{2+} in biological samples after some additional studies.

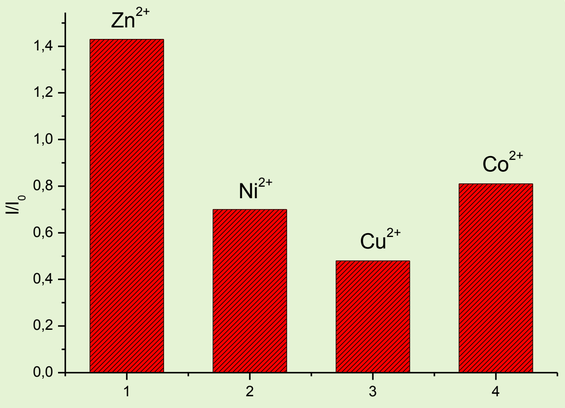


Figure 5. The selectivity of chemosensors 3 towards metal cations

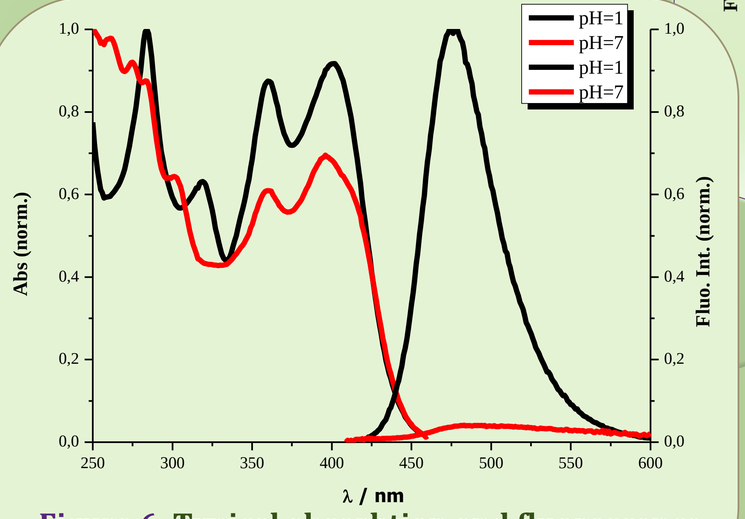


Figure 6. Typical absorbtion and fluorescence emission spectra of neutral and protonated species of compound 6

All of the examined compounds exhibited spectral changes in the pH range 1-12. Batochromic shift of the fluorescence emission band and strong increase of fluorescence intensity of compounds 3, 4 and 5 occurs on its exposure to acidic solution. It is found that compounds 3-6 have potential for application in acidic environments (pK_{app} are in range 2.70 – 3.45).