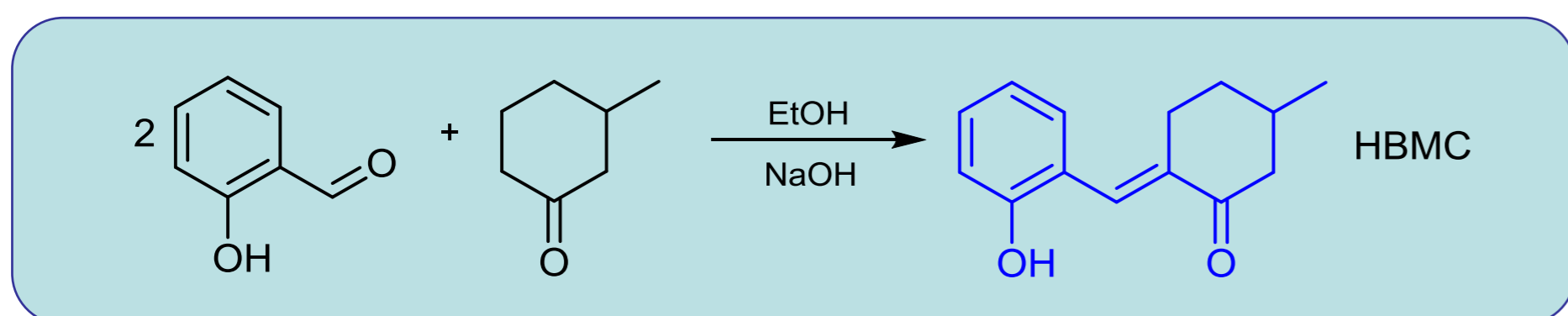


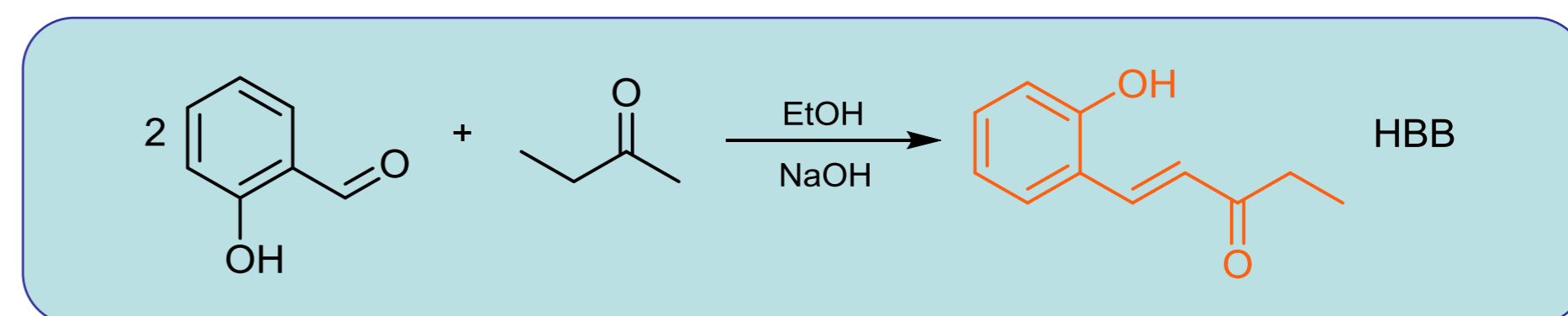
## Introduction

The development of novel photochromic systems capable of existing in more than two forms when subjected to different external stimuli has gained an increased interest in the last decades due to their industrial applications in optical memory devices, sensors, switches, intelligent windows and displays [1-4].

As a continuous work of our research group in the frame of multistate/multifunctional systems we report herein the synthesis, X-ray structure, spectral properties of 2-(2-hydroxybenzylidene)-5-methylcyclohexanone and 1-(2-hydroxybenzylidene)butanone and their behavior as a function of pH. Additionally kinetic information was achieved by carrying out direct and reverse pH jumps.



Synthesis of 2-(2-hydroxybenzylidene)-5-methylcyclohexanone (HBMC)



Synthesis of 1-(2-hydroxybenzylidene)butanone (HBB)

## Results and discussion

The HBMC compound was obtained by condensation reaction in basic alcoholic solutions from 2-hydroxybenzaldehyde and 3-methylcyclohexanone. The <sup>1</sup>H NMR experiments were recorded in DMSO-*d*<sub>6</sub> and CD<sub>3</sub>OCD<sub>3</sub> and proved the structure (Fig.1).

X-ray single crystal study demonstrated that compound HBMC has a molecular crystal structure built up from neutral units, as shown in Fig. 2.

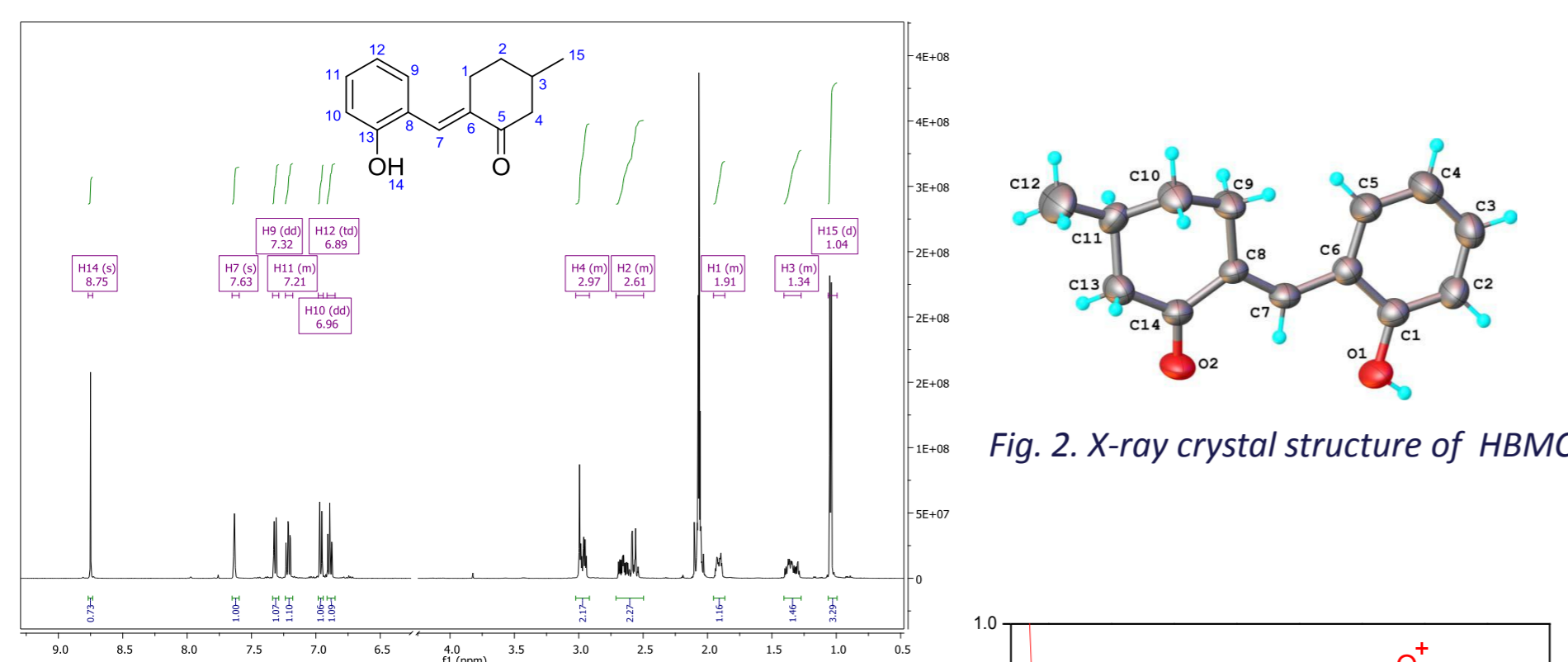


Fig. 2. X-ray crystal structure of HBMC

Fig. 1. <sup>1</sup>H-NMR spectrum of HBMC in DMSO-*d*<sub>6</sub>

In acidic conditions the solution of HBMC changed from pale yellow to red due to the formation of the cationic form with a maximum absorption at 515 nm (Fig. 3).

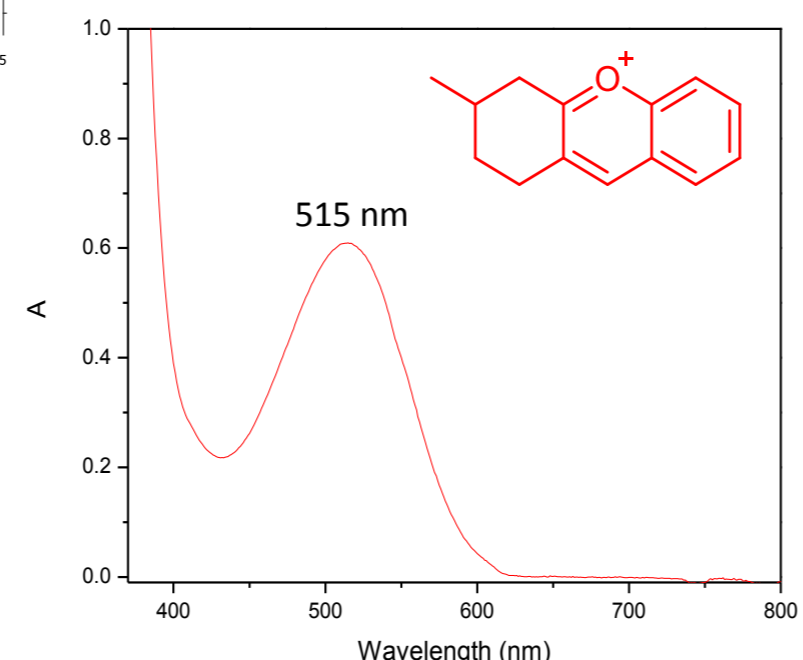
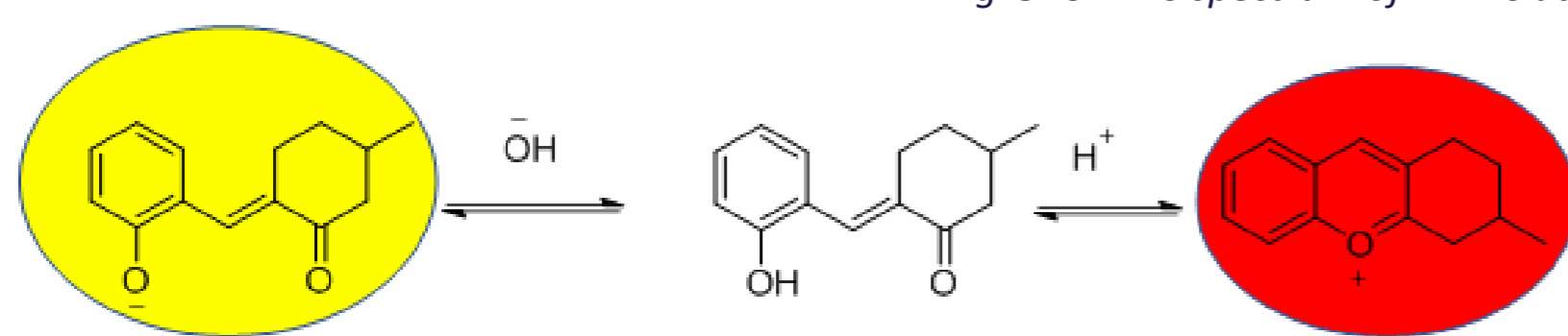


Fig. 3. UV-VIS spectrum of HBMC at acidic pH



Scheme 1. Network of chemical reactions

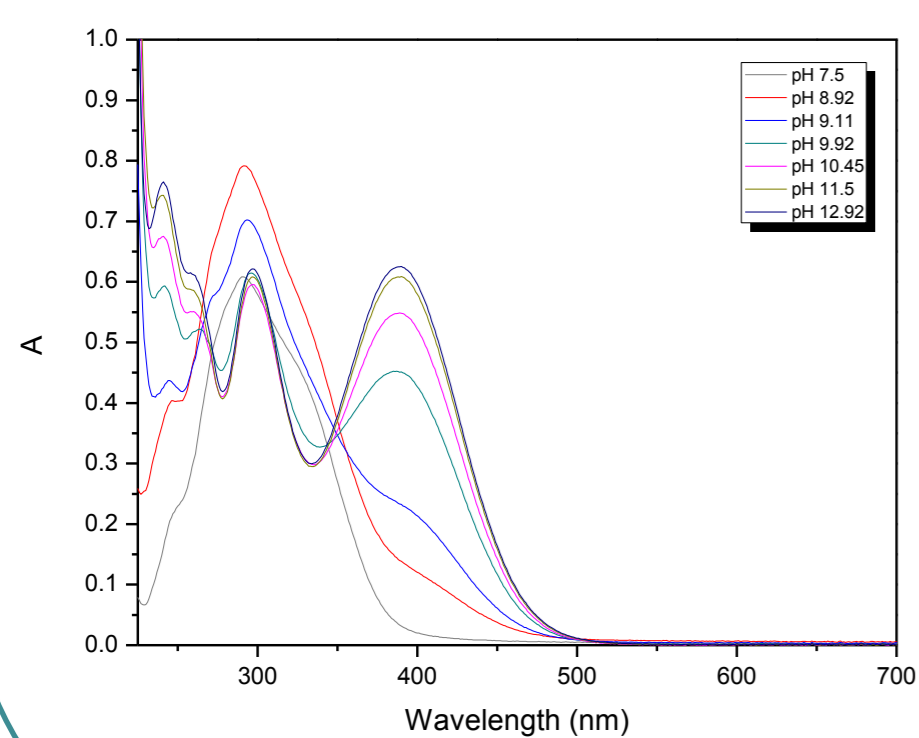


Fig. 4. UV-Vis spectra of HBMC in basic pH

In basic conditions the HBMC turns into the unprotonated form (HBMC<sup>-</sup>) which exhibits a broad absorption band at 390 nm (Fig. 4). The intensity of the absorption band characteristic to the HBMC<sup>-</sup> anion was gradually increased with the pH and the saturation was observed around pH 13, as the acido-basic equilibrium presented in Scheme 1 is drastically shifted to the left.

## Results and discussion

The HBB compound was obtained by condensation reaction in basic alcoholic solutions from 2-hydroxybenzaldehyde and butanone. The HBB structure was confirmed by NMR spectroscopy (Fig. 5).

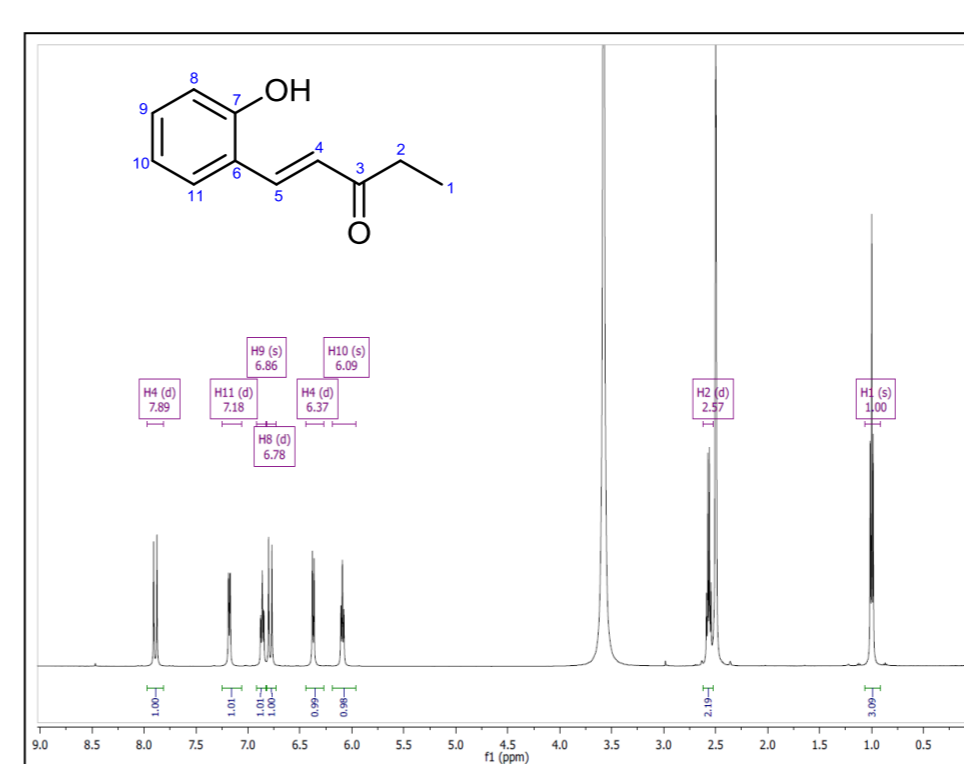


Fig. 5. <sup>1</sup>H-NMR spectrum of HBB in DMSO-*d*<sub>6</sub>

At very low pH values the HBB turns into cationic form with orange color and a maximum absorption at 442 nm and 304 nm (Fig. 7).

The kinetics of the direct pH jumps from 1.5 to 12.2 is presented in Fig. 6. After a direct pH jump to 12.2, the unprotonated form is formed with a maximum absorption at 384 nm. This is followed by a kinetic process represented in Fig. 6.

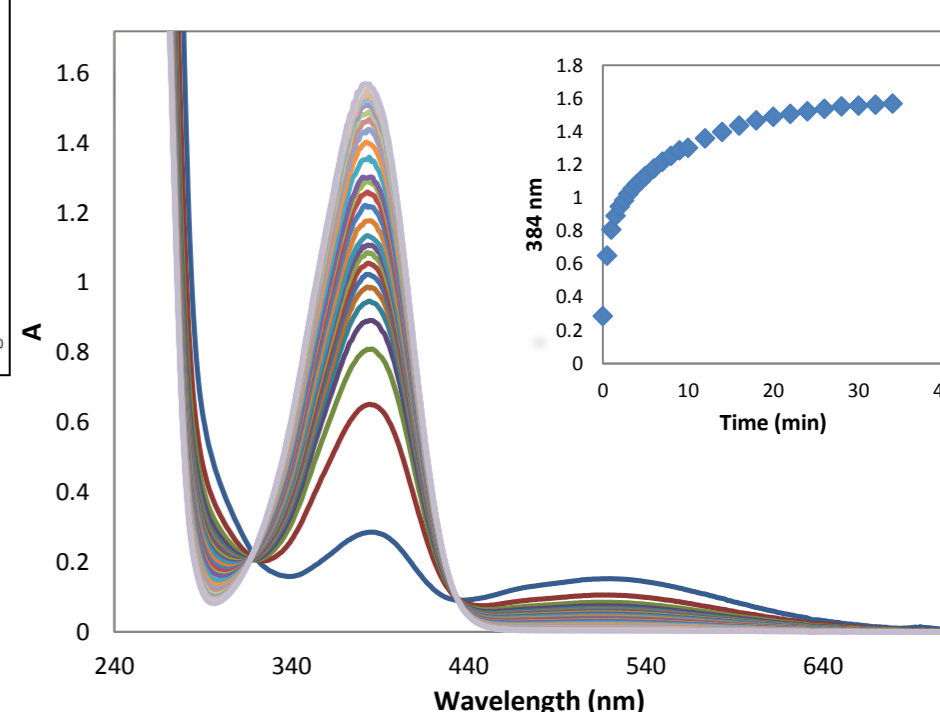
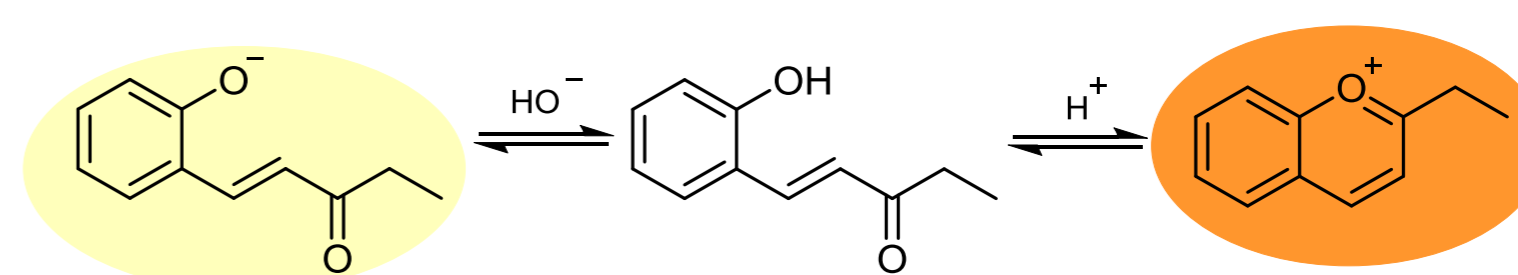


Fig. 6. Spectral variations of HBB after a direct pH jump from pH=1.5 to pH=12.2



Scheme 2. Proposed network of chemical reactions

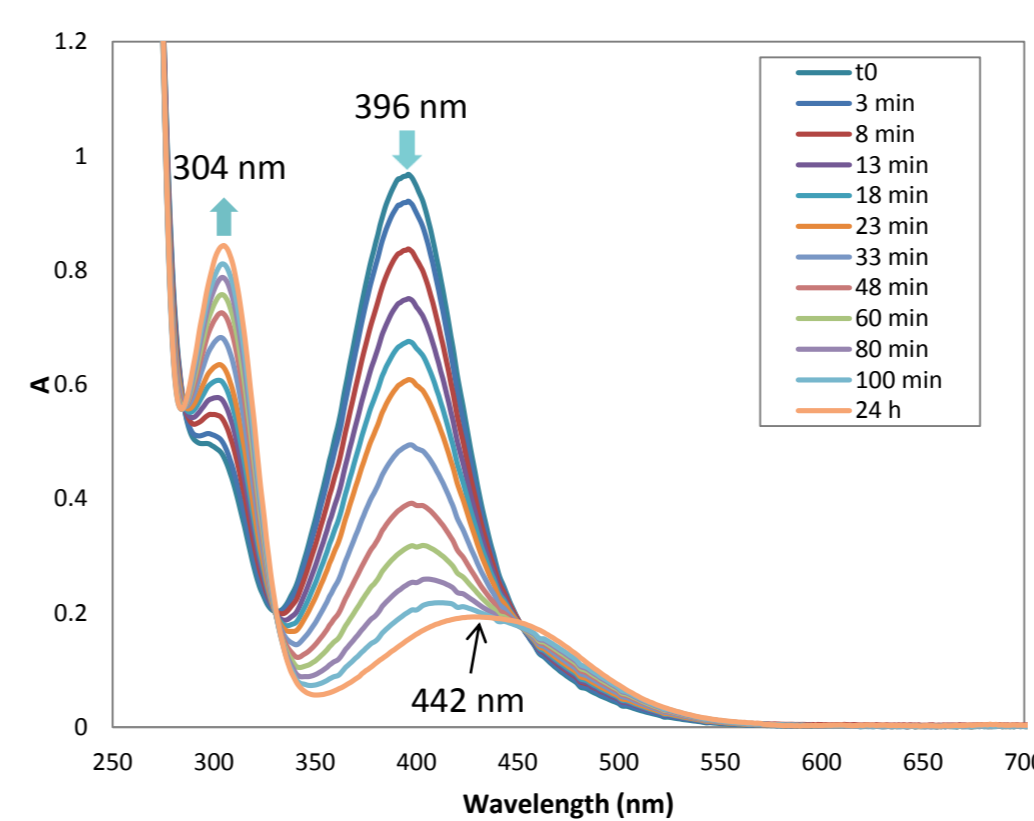


Fig. 8. Spectral variations of HBB after reverse pH jump 3.7 < pH < 1.3

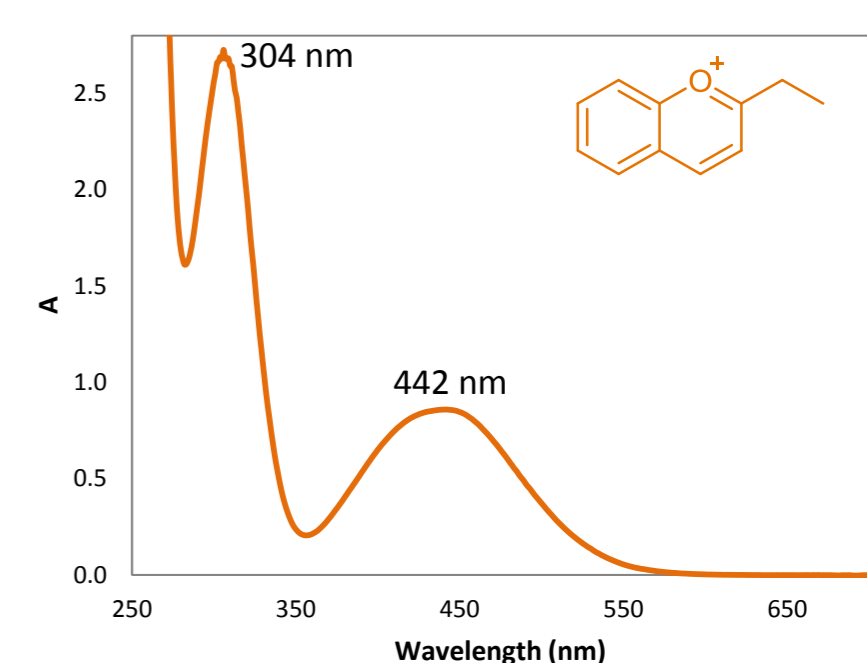


Fig. 7. UV-VIS spectrum of HBB at pH 0.5

The absorption spectra of HBB taken after reverse pH jump from an equilibrated solution at pH 3.7 to 1.3 is presented in Fig. 8. The reverse pH jump shows the formation in time of the cationic species with the characteristic absorption bands at 442 nm and 304 nm.

## Conclusions

- ✓ New hydroxybenzylidene derivatives has been synthesized and characterized by NMR spectroscopy;
- ✓ pH dependent photochromic behavior of HBMC and HBB in acid and basic environment was assessed using UV-Vis spectroscopy;
- ✓ X-ray diffraction of HBMC shows a monoclinic packing of crystal system with 4 molecules/unit cell;
- ✓ The detailed kinetic studies of HBB after direct and reverse pH jumps permit to identify the species present at each pH value.

## Acknowledgements

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