

## Supplementary material

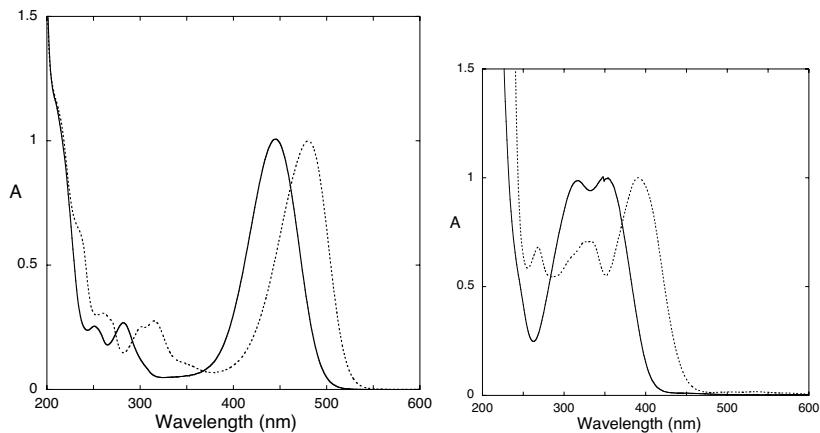


Fig. 1S Normalized absorption spectra of 4'-Hydroxyflavylium (full line) and 4'-Hydroxynaphthaloylium (pointed line).

## Flash Photolysis

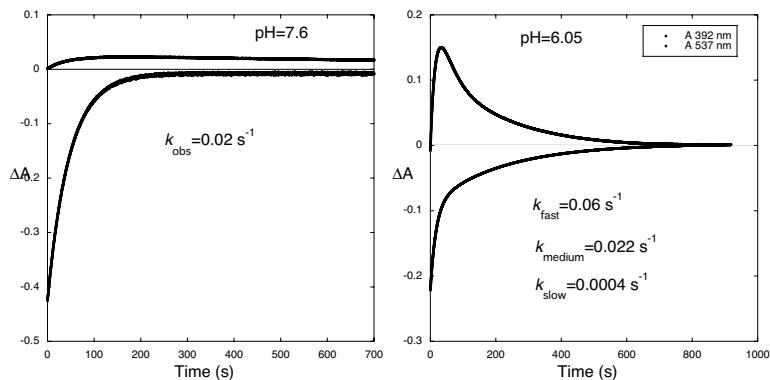


Fig. 2S. Flash photolysis traces

At pH=7.6 the observed process after the flash is essentially the recovering of **Ct** form **CC** in equilibrium with **B**, assuming that this equilibrium takes place in the time scale of sub-seconds as observed for similar compounds.  $\chi_{C_c} k_i = 0.02 \text{ s}^{-1}$  leading to  $k_i = 0.04 \text{ s}^{-1}$ .

At pH= 6.05 we are observing three processes. The fast one is the formation of **A** together with some **Ct** recovery, as observed in other cases. Regarding the other two kinetics, they correspond to the hydration  $\chi_{AH+} k_h$  (medium process) and isomerization (slower process).

### Fluorescence

The fluorescence emission of the compound at the maximum of the  $\text{AH}^+$  absorption,  $\lambda_{\text{exc}}=480 \text{ nm}$ , leads to an emission which is a mirror image of the absorption and a relatively small Stokes shift indicating a small distortion of the  $\text{AH}^+$  excited state. It is worth of note that no emission could be detected immediately after a pH jump from equilibrated solutions at pH=1 to 6.8, indicating that the quinoidal base does not emit.

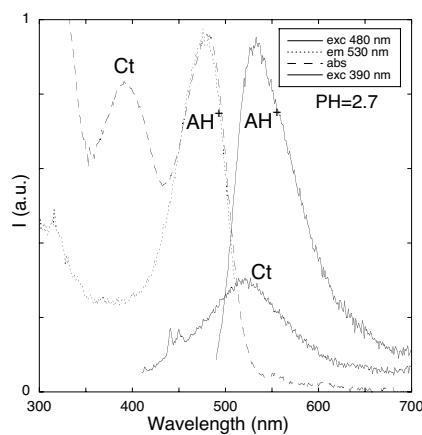


Fig.3S- Normalized fluorescence emission spectra at pH=2.7 and  $\lambda_{\text{exc}}=480 \text{ nm}$  and 390 nm ( $\text{AH}^+$  and Ct emission respectively) (solid lines). Excitation ( $\lambda_{\text{em}}=530 \text{ nm}$ ) (dotted line) and absorption spectra (dashed line) of the same solution.

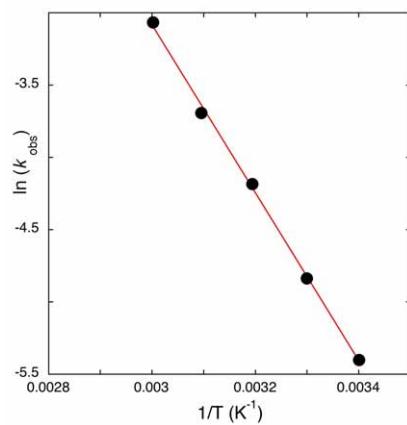


Fig. 4S. Arrhenius plot of the isomerization process taking place after pH jumps from 1.0 to 6.0. Activation energy equal to 48  $\text{kJmol}^{-1}$ .

