

## Picosecond Excited State Proton Transfer Dynamics of a Pyranoflavylum Salt in Methanol-Water Mixtures

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Pyranoanthocyanins are pigments formed in aged red wines through condensation of anthocyanins with acetaldehyde, pyruvate or vinyl phenol produced during the fermentation process.<sup>[1]</sup> They are characterized by an enhanced color stability against hydration or bleaching by sulphur dioxide in comparison with their respective anthocyanin precursors.<sup>[1,2]</sup>

In this work, the excited state proton transfer reaction (ESPT) has been investigated by employing the synthetic pyranoflavylum cation 8-hydroxy-5-phenyl-2-(4-methoxyphenyl)-1,6-dioxaphenalene chloride (HAPF, Fig. 1a), prepared as described<sup>[1]</sup> by the condensation of the 5,7-dihydroxy-4-methylflavylium chloride with *p*-methoxybenzaldehyde.

Because HAPF is sparingly soluble in water, in clear contrast with most flavylum salts, the ESPT was studied in 30% (v/v) methanol-water (mole fraction of methanol = 0.16) as a function of pH. In 30% (v/v) methanol-water at 20 °C, the fluorescence decays were double exponential, indicating that the ESPT mechanism involves solely the first singlet excited states of HAPF in its acid (AH<sup>+</sup>\*) and conjugate base A\* forms, as depicted in Fig. 1b.

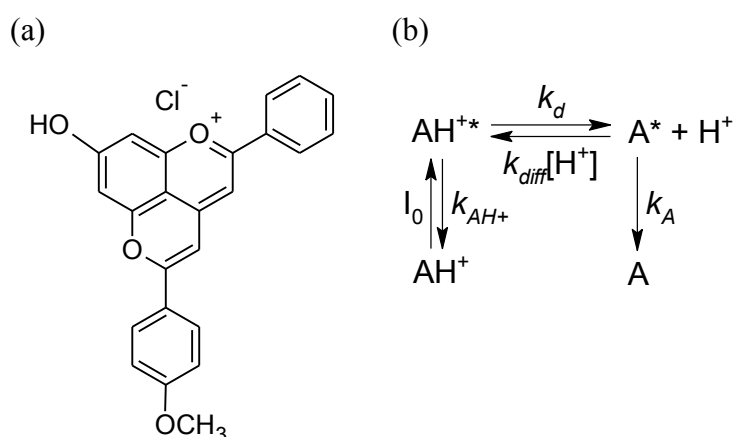


Figure 1. a) Chemical structure of the pyranoflavylum salt HAPF, b) scheme of the ESPT kinetics observed in 30% methanol-water (v/v) for HAPF as a function of pH at  $T = 20$  °C.

The AH<sup>+</sup>\* form deprotonates in *ca.* 650 ps, much slower than the typical values of 5-20 ps observed for the ESPT of synthetic flavylum salts and natural anthocyanins in diverse media

such as water, water-organic solvent mixtures, or cationic and nonionic micelles.<sup>[3,4]</sup> The excited-state lifetime of the conjugate base A\* is *ca.* 950 ps, also longer than the 120-260 ps range found for A\* of flavylum salts and anthocyanins. In pure methanol containing 0.6 M trifluoroacetic acid, the deprotonation of AH<sup>+</sup>\* does not take place and the fluorescence decay of AH<sup>+</sup>\* is monoexponential with a lifetime of 2.4 ns.

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