

The photoacidity of indolinobenzospiropyrans in water

C. Pezzato

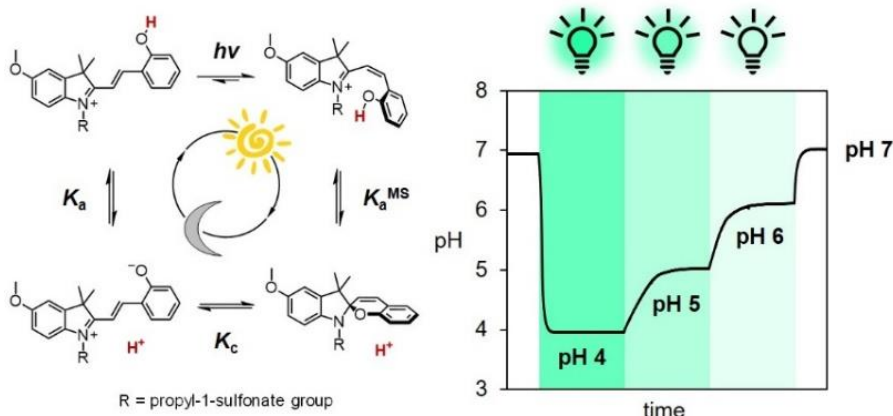
Institute of Chemical Sciences and Engineering,

Swiss Federal Institute of Technology in Lausanne (EPFL), Switzerland.

cristian.pezzato@epfl.ch

The reversible UV light-triggered ring-opening reaction of indolinobenzospiropyrans (SPs) has been studied and applied extensively in the past decades, but mostly in organic solvent mixtures. The aqueous equilibrium distribution of SPs in the ground state, though, involves three different isomers and can be quantitatively shifted towards their open protonated forms (MCHs) depending on the pH of the solution. It follows that SPs in water can display *negative* photochromism [1] – i.e., visible light-triggered ring-closing reaction coupled with proton release [2]. In this talk, I will discuss our latest advances in the physicochemical characterization and application of MCHs in water. Recently, we rationalized the thermodynamics and kinetics of MCHs through cross-validation of ^1H NMR, UV-Vis, and pH measurements [3]. We demonstrated that, under dark conditions, they are organic weak acids displaying ground state acidity constants close to neutrality ($\text{p}K_{\text{a}} = 6\text{--}7$), whereas,

under visible light irradiation, they become more acidic by ca. 4 pK units ($\text{p}K_{\text{a}}^* = 2\text{--}3$). Specifically, we showed that the proton release of MCHs in water is quantitatively described by a four-state dynamic model. We also showed that partial neutralization of aqueous solutions of



MCHs with a base allows for carefully tuning i) their pH in the dark according to the Henderson-Hasselbalch equation and ii) the pH jump following visible light absorption up to 3 pH units [4], and that the photoacidity of MCHs increases with decreasing temperature [5]. Finally, I will discuss how both the hydrolytic stability and the pH jumps of MCHs can be dramatically enhanced by supramolecular encapsulation with cucurbiturils, and I will show how MCHs can be used to control pH-sensitive DNA nanoswitches.

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References. [1] L. Kortekaas, W. R. Browne, *Chem. Soc. Rev.*, **2019**, *48*, 3406-3424; [2] Y. Liao, *Acc. Phys. Chem. Chem. Phys.*, **2022**, *24*, 4116-4124; [3] C. Pezzato *et al.*, *Chem. Sci.*, **2020**, *11*, 8457-8468; [4] C. Pezzato *et al.*, *Angew. Chem. Int. Ed*, **2021**, *60*, 21737-21740; [5] C. Pezzato *et al.*, *Mater. Today Chem.*, **2022**, Accepted.