

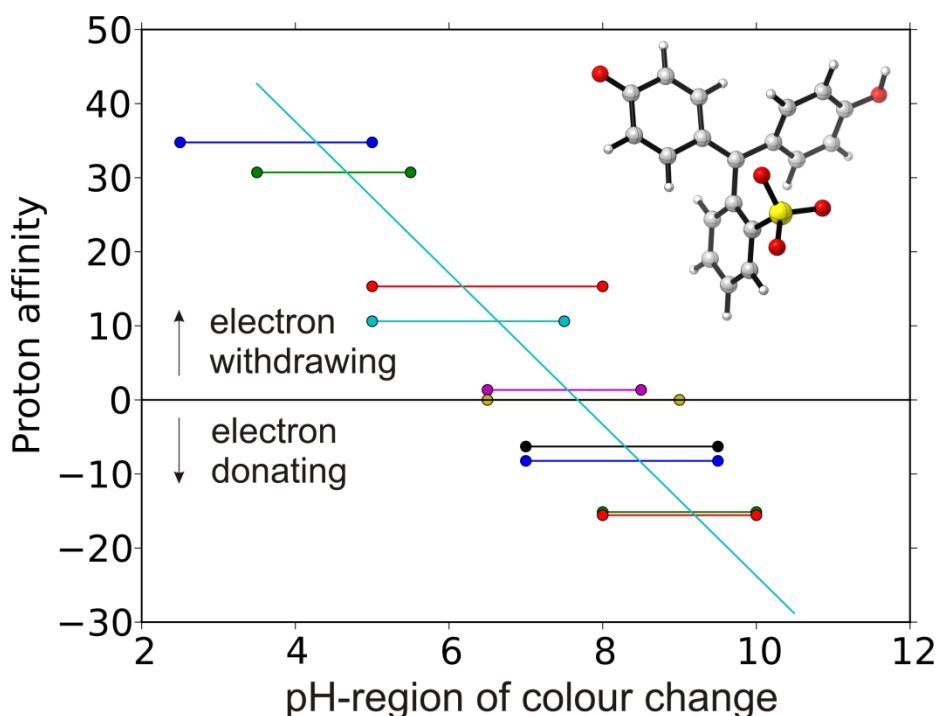
## Substituent effects on absorption spectra of pH indicators: An experimental and computational study of sulfonphthaleine dyes

Sulfonphthaleine dyes are an important class of pH indicators, finding applications in novel (textile) sensors. The goal of this combined theoretical and experimental research is to understand the effect of substituents on the halochromic properties of a large set of sulfonphthaleine compounds.<sup>1</sup>

Starting from an experimental analysis consisting of UV/Vis spectroscopy, the pH region and the absorption wavelengths related to the colour shift are obtained and  $pK_a$  values are derived. The effect of the substituents on the pH region can be traced back to their electron donating/withdrawing properties. These results are then cross-validated with quantum mechanical computations to gain a more in-depth view of the underlying mechanisms.

Time-Dependent Density Functional Theory (TD-DFT) is able to adequately produce the trend in experimental wavelengths.<sup>2</sup> Proton affinities are used to assess the effect of substituents on the pH region and a linear correlation is found (see Figure).

The combination of theory and experiment is able to give a better understanding of the pH sensitivity; the methodology in this work will be useful in future dye design and is applicable to other dye classes as well. This knowledge can also help subsequent research to achieve more insight into the influence of a textile matrix on the halochromic properties of pH indicators.



*A clear linear correlation between theoretical proton affinities and the  $pK_a$  (pH-region of the colour change) is found.*

<sup>1</sup> T. De Meyer et al. *Chemistry – A European Journal* 18 (26), 8120-8129 (2012).

<sup>2</sup> D. Jacquemin et al. *International Journal of Quantum Chemistry* 112 (9), 2135-2141 (2012).