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

T. De Meyer[a], K. Hemelsoet[a], K. De Clerck[b], V. Van Speybroeck[a]
[a]CMM, Ghent University, Technologiepark 903, Zwijnaarde; e-mail: thierry.demeyer@ugent.be; [b]Department of Textiles, Ghent University, Technologiepark 903, Zwijnaarde; e-mail: karen.declerck@ugent.be

Abstract

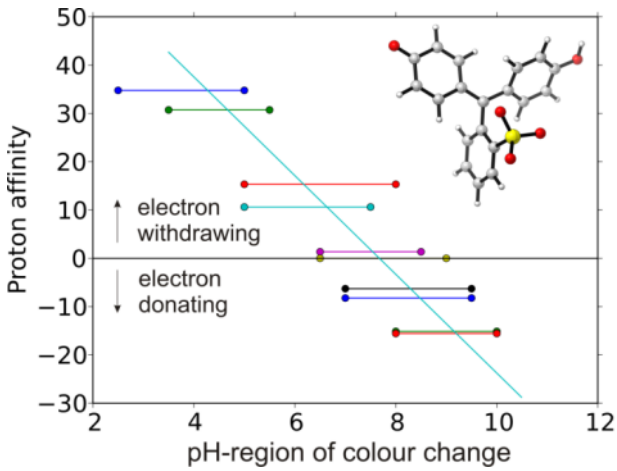
Besides their original use as colourants, dyes are increasingly applied in other fields, such as photovoltaic cells, optical switches and light emitting diodes [1]. Some dyes show chromic properties, meaning that they change colour depending on an external influence [2]. We are mainly interested in pH-sensitive behaviour since our main interest lies in the possible application of dyes in pH-responsive polymers, or more precisely intelligent textiles. Sulfonphthaleine dyes are an important class of pH indicators.

These novel textile sensors maintain all advantages of textile materials, meaning they are flexible, applicable on large surfaces and can give a local discolouration. This colour change is easy to perceive and can be used as a first warning signal. 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 [3].

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 [4]. Especially when combined with quantum mechanical/molecular mechanical (QM/MM) molecular dynamic simulations, as shown in a previous study for the azo dye Ethyl Orange [5]. 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.



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