The pH-sensitive properties of azo dyes in aqueous environment

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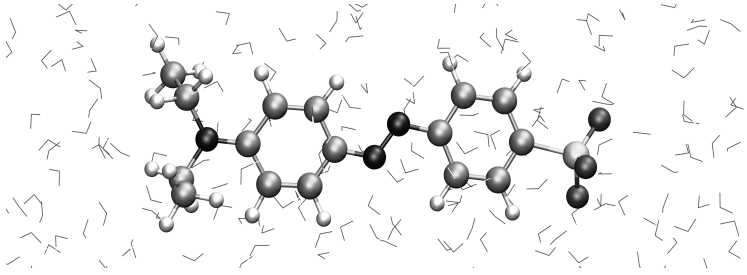
ABSTRACT Azo dyes consist of a double nitrogen-nitrogen bond connected to two aromatic moieties, creating a large conjugated π-system. A relatively simple synthesis and large variety of colours have made azo dyes the most abundant class of colourants. The dye studied in this research, ethyl orange (**EO**), is a prototypical example of a halochromic (pH-sensitive) azo dye. Halochromic dyes have already proven useful for application in textile sensors since the colour change of such sensors is easy to perceive and the advantages of the parent materials (e.g. flexibility) are maintained.[1] The key to further development of smart materials is combining multiple responses that can be separately addressed by different triggers.[2] To achieve this, we need a full knowledge of the colour changing mechanism and the influence of the environment. Herein, both theoretical and experimental methods were used to unravel the halochromic properties of **EO**.[3]

Experimental UV-VIS and Raman spectra point towards a structural change of **EO** in water between pH 5 and pH 3. This pH-sensitivity is modeled through a series of ab initio computations on the neutral, various singly and doubly protonated structures. Static calculations (with inclusion of implicit solvation) are successful in assigning the most probable protonation site. However, to fully understand the origin of the main absorption peaks, a molecular dynamics simulation study in a water molecular environment is used in combination with Time Dependent-DFT calculations to deduce average UV-VIS spectra which take into account the flexibility of the dye and the explicit interactions with the surrounding water molecules. The proposed methodology allows to achieve a remarkable agreement between the theoretical and experimental UV-VIS spectrum and enables to fully unravel the pH sensitive behaviour of **EO** in aqueous environment.



References:

[1] Van der Schueren, L. and De Clerck, K. *Textile Research Journal* 80(7) (*2010*) 590-603.

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