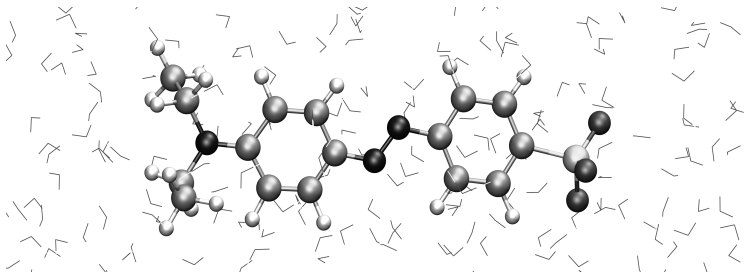
UV-VIS spectra of azo dyes in aqueous environment: a combined TD-DFT and molecular dynamics study

Thierry De Meyer,[1,2] Karen Hemelsoet,[1] Lien Van der Schueren,[2] Ewald Pauwels,[1] Karen De Clerck,[2] Veronique Van Speybroeck[1]

[1] *Center for Molecular Modeling, Ghent University, Technologiepark 903, 9052 Zwijnaarde, Belgium; QCMM-Alliance Ghent-Brussels, Belgium and* [2] *Department of Textiles, Ghent University, Technologiepark 907, 9052 Zwijnaarde, Belgium*
thierry.demeyer@ugent.be

ABSTRACT The goal of this research is to unravel the pH-sensitive behaviour of azo dyes with the use of Time Dependent Density Functional Theory (TD-DFT) and molecular dynamics (MD) simulations.[1] Starting from an experimental analysis, an increasingly advanced description of the molecular environment is taken into account. To generate accurate geometries, the popular hybrid B3LYP functional was initially chosen. The results were cross-validated with more recent functionals that include dispersion interactions, in particular CAM-B3LYP and M06, which are promising in the description of delocalized systems.[2] In vacuo calculations were successful in assigning the most probable protonation site. Electronic excitation wavelengths were calculated using TD-DFT on the neutral dye and various singly and doubly protonated structures. All three DFT functionals were successful in reproducing the experimental trend in the UV-VIS spectra.

To include a water solvent in the calculations, two approaches were used. The first and computationally least demanding way is to use an implicit solvation model.[2] The excitation wavelengths calculated with PCM-B3LYP were closest to experimental data. However, to fully understand the origin of the main absorption peaks, a hybrid molecular dynamics simulation study in a water molecular environment is used in combination with TD-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. This 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 azo dyes in aqueous environment.



References:

[1] De Meyer, T. et al. *Chemistry - A European Journal* in press (DOI 10.1002/chem.201103633).

[2] Jacquemin, D. et al. *International Journal of Quantum Chemistry* 110(12) (*2010*) 2121-2129.