pH-sensitive dyes in aqueous solution

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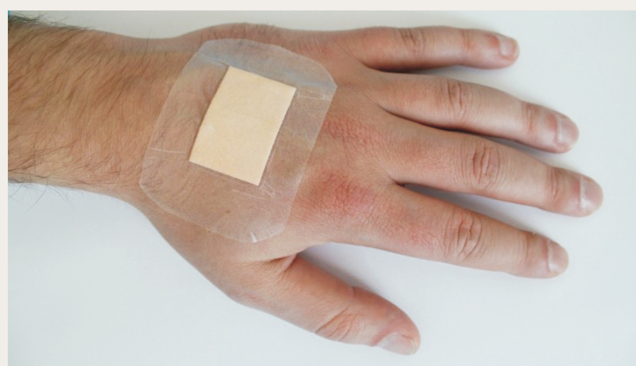
pH-sensitive dyes and their applications

Halochromic dyes are very promising for developing new sensor materials. They can easily be applied to polymer matrices using conventional textile dying processes,[1] while covalent bonds provide a different route.

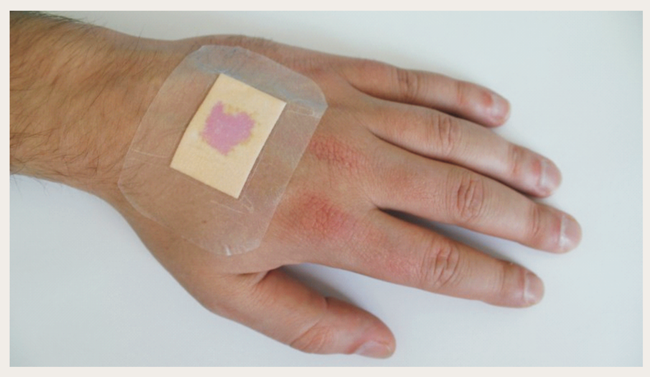
pH-sensitive polymers:
- colour change is easy to perceive
- benefits of parent materials (e.g. flexibility)
- possible application: wound dressings[1]

Computational research is essential to gain a better understanding of the influence of the environment on the halochromic behaviour.

The knowledge obtained in this research can be useful for dyes sensitive to other external stimuli (thermochromism, solvatochromism, ...)



↓ Infection



Computational Strategy

Molecular structure/Periodic unit cell

↓

Optimization/Molecular Dynamics (MD)[2]

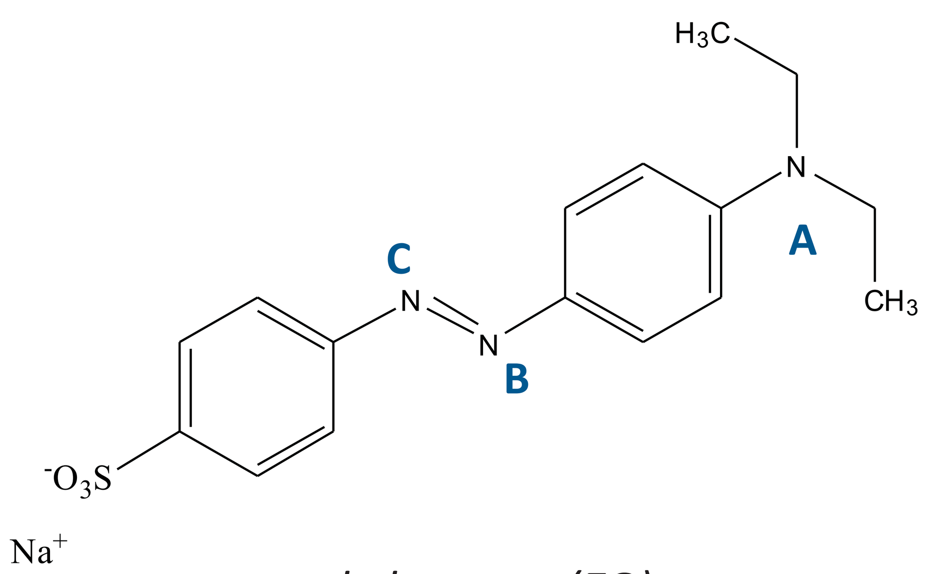
↓

Calculation of spectroscopic properties[3]

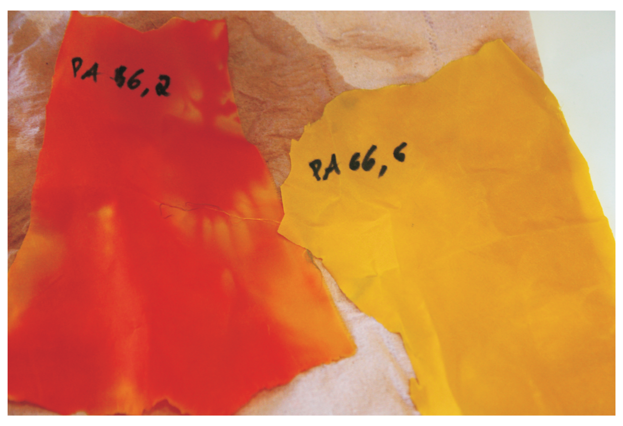
↓

Interpretation and analysis of spectra/ Comparison with experiment

Halochromic behaviour of ethyl orange (EO)

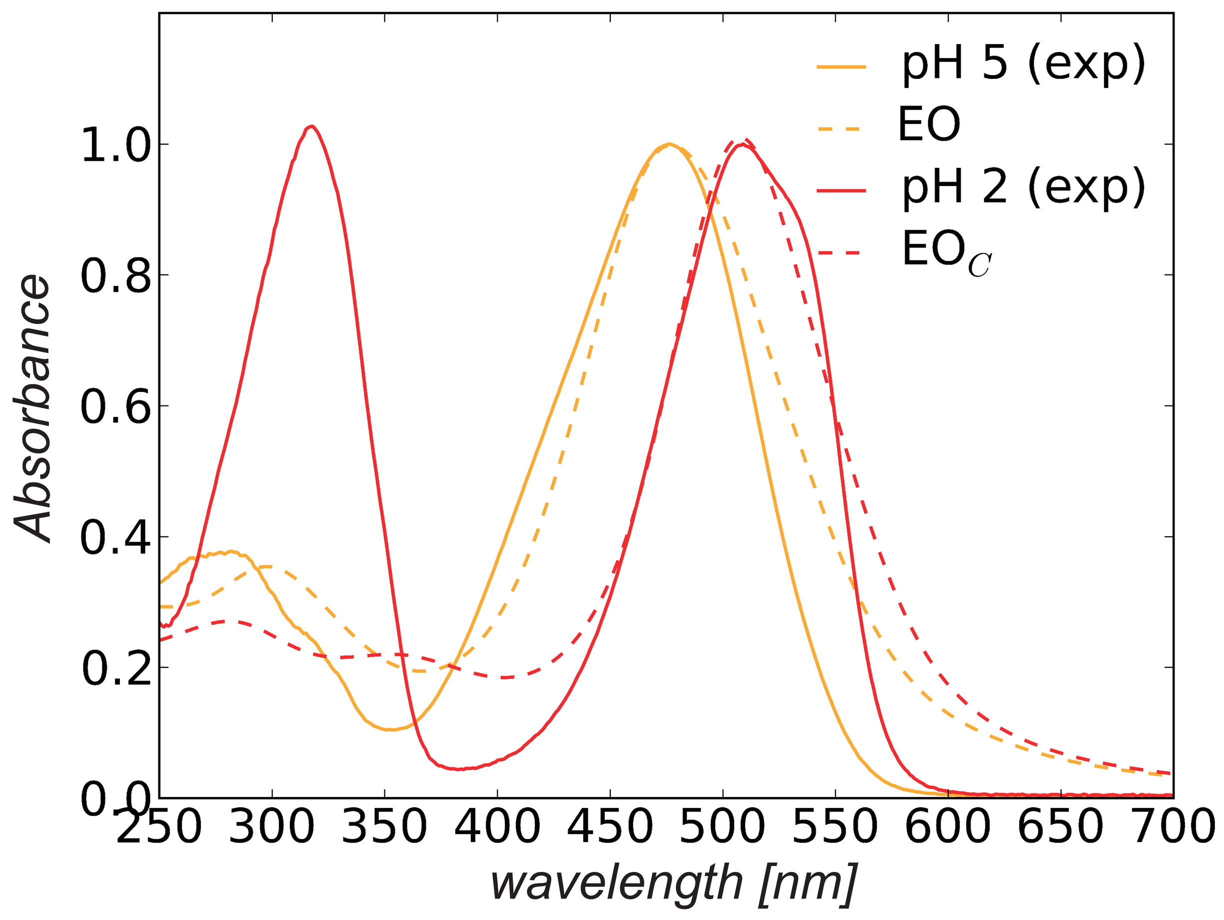


*ethyl orange (**EO**)*



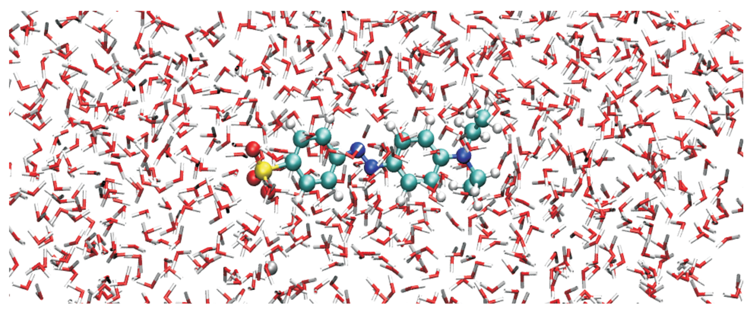
***EO** dyed onto PA6.6 at low pH (left) and high pH (right)*

UV-VIS spectra of EO (aqueous solution)



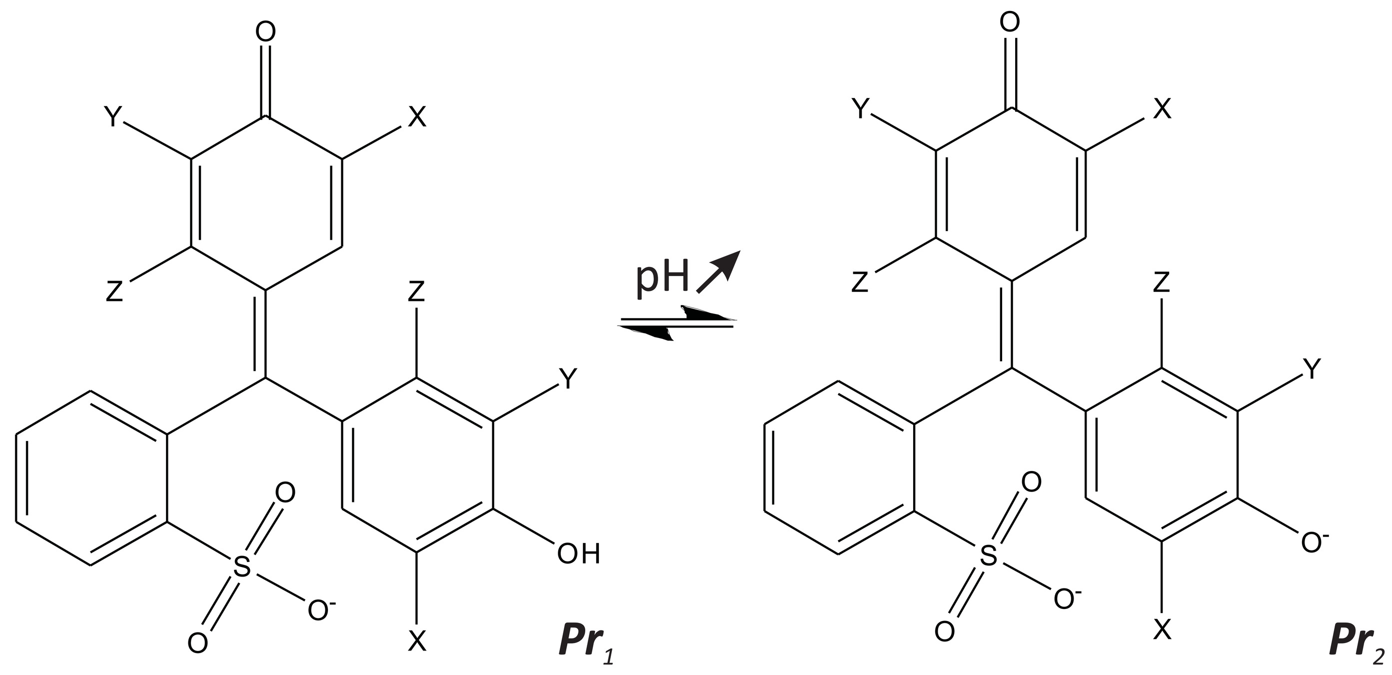
Experimental UV-VIS spectrum of **EO** in water shows a peak shift in the visual area between 473 nm and 508 nm when the pH drops from 5 to 3. This is accurately reproduced by calculated spectra based on MD simulations.[4]

MD-methodology:
- 5 ps QM/MM simulation (BLYP + TIP3P water)
- B3LYP/6-31+G(d,p) TD-DFT IEF-PCM calculation on the extracted dye molecule on 100 snapshots
- Averaging over the different spectra



nm (eV)	EO	EO_C	
Exp	473 (2.62)	508 (2.44)	
B3LYP	453 (2.74)	470 (2.64)	static
M06	441 (2.81)	462 (2.68)	static
CAM-B3LYP	392 (3.16)	441 (2.81)	static
MD - B3LYP	476 (2.61)	508 (2.44)	dyn

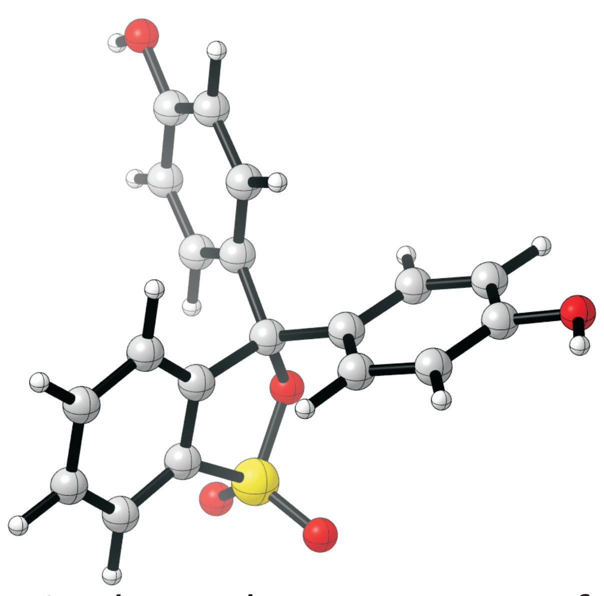
Halochromic behaviour of phenol red (PR) and derivatives



*In water, singly deprotonated phenol red (**PR**$_1$) undergoes a second deprotonation (**PR**$_2$) in alkalic media. This mechanism causes the colour change from yellow to red.*

nm (eV)	Cresol Red (**CR**) X=CH_3, Y=Z=H		Xylenol Blue (**XB**) X=Y=CH_3, Z=H		Chlorophenol Red (**ChR**) X=Cl, Y=Z=H		Bromocresol Purple (**BP**) X=Br, Y=CH_3, Z=H		Bromothymol Blue (**BB**) X=*i*-Pr, Y=Br, X=CH_3	
	CR_1	**CR_2**	**XB_1**	**XB_2**	**ChR_1**	**ChR_2**	**BP_1**	**BP_2**	**BB_1**	**BB_2**
Exp	437 (2.84)	573 (2.16)	437 (2.84)	546 (2.27)	436 (2.84)	575 (2.16)	432 (2.87)	589 (2.11)	435 (2.85)	617 (2.01)
B3LYP	428 (2.90)	496 (2.50)	442 (2.81)	523 (2.37)	426 (2.91)	492 (2.52)	423 (2.93)	506 (2.45)	461 (2.69)	548 (2.26)
M06-2X	362 (3.43)	484 (2.56)	368 (3.37)	480 (2.58)	374 (3.32)	502 (2.47)	402 (3.08)	522 (2.38)	380 (3.26)	493 (2.52)

nm (eV)	Phenol Red (**PR**) X=Y=Z=H	
	Pr_1	**Pr_2**
Exp	433 (2.86)	559 (2.22)
PBE0	411 (3.02)	473 (2.62)
B3LYP	421 (2.95)	484 (2.56)
M06-2X	374 (3.32)	473 (2.62)
CAM-B3LYP	368 (3.37)	465 (2.67)



*Optimized gas phase structure of **PR***

For the singly deprotonated form (**PR**$_1$), both PBE0 and B3LYP provide accurate results, with the latter being slightly better. While B3LYP results are still closest to experiment for the doubly deprotonated form (**PR**$_2$), all functionals show a great discrepancy with experiment. The main reason for this is probably the double negative charge. Also note that the Coulomb-attenuated B3LYP performs much worse than it's non-attenuated version

Conclusions and future work

The combined MD/static approach used in this work provides a viable route into accurately calculating UV/Vis spectra.

Molecules with a double negative charge (such as **PR**$_2$) still pose a problem and need a more accurate description.

Besides vertical transitions, adiabatic transitions are also being examined.

Halochromic properties will also be studied in a polymer/textile enviroment, both experimentally and theoretically.

References

[1] Van der Schueren, L. and De Clerck, K. *Textile Research Journal* 80(7), 590-603 (2010).
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[3] Adamo, C. and Jacquemin, D. *Chemical Society Reviews* 42(3), 845-856 (2013).
[4] De Meyer, T et al. *Chemistry - A European Journal* 18 (26) 8120-8129 (2012).