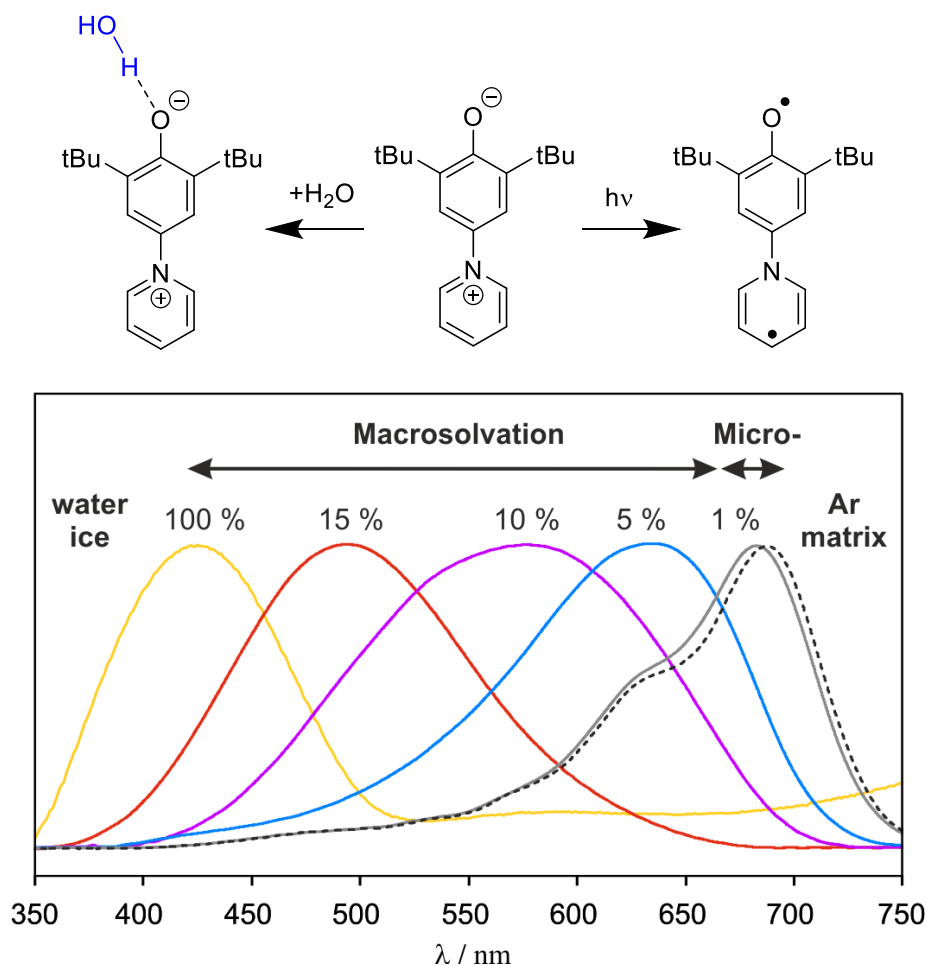


Micro- vs Macrosolvation in Reichardt's Dyes

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Solvation is a complex phenomenon involving electrostatic and van der Waals forces as well as chemically more specific effects such as hydrogen bonding. To disentangle global solvent effects (macrosolvation) from local solvent effects (microsolvation), we studied the UV-vis and IR spectra of a solvatochromic pyridinium-N-phenolate dye (a derivative of Reichardt's dye) in rare gas matrices, in mixtures of argon and water, and in water ice at 3 K. The π - π^* transition of the betaine dye in the visible region and its C–O stretching vibration in the IR region are highly sensitive to solvent effects. By annealing argon matrices of the betaine dye doped with low concentrations of water, we were able to generate 1:1 water-dye complexes. Formation of hydrogen-bonded complexes leads to small shifts of the π - π^* transition only, as long as the global polarity of the matrix environment does not change. In contrast, changes of the global polarity result in large spectral band shifts. Hydrogen-bonded complexes of the betaine dye are more sensitive to global polarity changes than the dye itself, explaining why empirical solvent polarity values ET determined with Reichardt's dyes are very different for protic and nonprotic solvents, even if the relative permittivities of these solvents are similar.



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