Effect of solvation on excited state symmetry breaking using transient infrared spectroscopy

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Over the past few years, two-branched symmetric electron donor-acceptor-donor (D-π-A-π-D) chromophores have been shown to undergo excited-state symmetry breaking (ES-SB) in polar environments. During this process, electronic excitation becomes unevenly distributed over the two DA branches and is highly dependent to the solvent polarity and the solvation dynamics [1]. In this work we will present the effects of solvation on the ES-SB, using a DAD chromophore in non-polar/polar solvent mixtures of different volumetric ratios. To do this, we use transient infrared (TRIR) spectroscopy, where we excite the sample at 400nm to the S1 state and probe the -C≡C-stretching vibrations of the excited molecule with broadband IR pulses as a function of the delay time.

Our results show that in pure non-polar solvents (CHX), the chromophore is excited to a symmetrical quadrupolar excited-state, where the charge transfer character is the same in both arms. Addition of a polar solvent (ACN), even in tiny amounts, results in a fluctuating solvent field around the chromophore. This leads to an uneven charge distribution around the molecule and a partial breaking of the symmetry, creating an Intermediate state where both antisymmetric and symmetric vibrational modes are visible (Figure 1 second panel). With a higher amount of polar solvent, the chromophore is surrounded by more polar molecules and the field becomes more asymmetric, leading eventually to a full localisation of the excitation in one arm and hence to a dipolar excited state D (figure 1 third panel). In pure polar solvent, the reaction field is even stronger and more asymmetric, the charge transfer only takes place in one arm and only the D state is visible.The time scales associated with the transitions between these states coincide with those of solvation dynamics, which involves significant translational diffusion in solvent mixtures

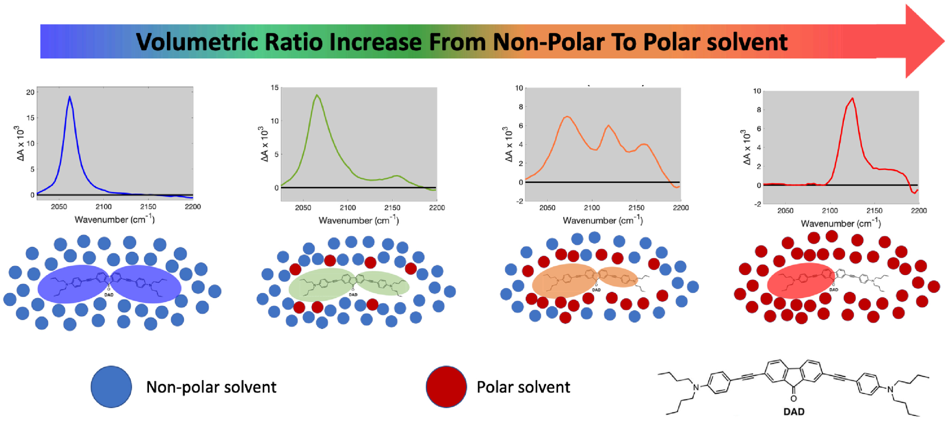

Figure 1. Transient infrared spectra of a DAD chromophore in non-polar/polar solvent mixtures (blue and red circles respectively). From left to right more polar solvent is added to the mixture and dipolar solvation starts taking place. This affects the environment around the chromophore breaking the symmetry, going from a symmetric quadrupolar state to a dipolar one.

[1]: B. Dereka, A. Rosspeintner, Z. Li, R. Liska, E. Vauthey, *J. Am. Chem. Soc.* **2016**, *138*, 4643-4649.