

Femtosecond transient absorption spectroscopy of photo- and thermo-switchable organic crystals

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Nonlinear optics (NLO) provides interesting properties such as second harmonic generation (SHG). The coupling between photochromism, thermochromism and NLO properties can be used in designing materials for new optical device for data storage or opto/thermo-switching. Salicylidene anilines (anils) are known to exhibit photochromism or thermochromism in the crystalline state (figure 1), and in at the same time some of them are SHG active in the crystalline state owing to a non centrosymmetric structure. 2-P, 4-P and 4-A fullfill these criteria (figure 2), and SHG could be reversibly photo-switched in 4-P and 4-A. Now our research is centred on the understanding of the origin and the dynamics of the properties' modulation.

In this work, we have investigated the photochromic reaction dynamics of 4-P in the crystalline state and solution by femtosecond transient absorption spectroscopy. It is the first study of this kind of anils in solid state. Under femtosecond photolysis, thermochromic 2-P yields transient species cis-keto* and cis-keto form. This behaviour is compared to 4-P and our results show that 4-P in crystalline state presents the similar photo-reaction kinetics to ethanol solution and formation of the photoproduct in crystalline state occurs in 200 ps (figure 3). Moreover an intermediate species obtained after proton transfer and before the formation of the photoproduct was observed, as predicted by theory¹. The photochromism was also studied by X-ray diffraction measurements, and a slight and reversible change of the crystal lattice was evidenced.

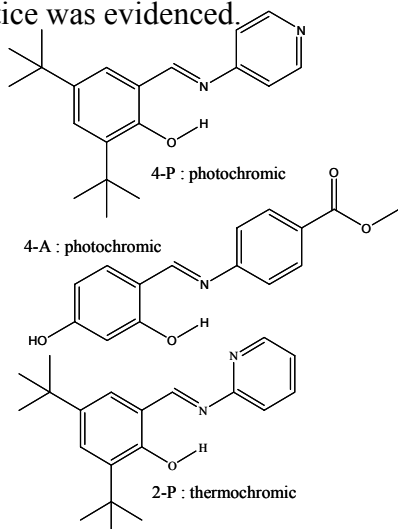


Figure 2: SHG active and thermo or photochromic anils in crystalline state

Figure 1: Photochromism and Thermochromism of anils

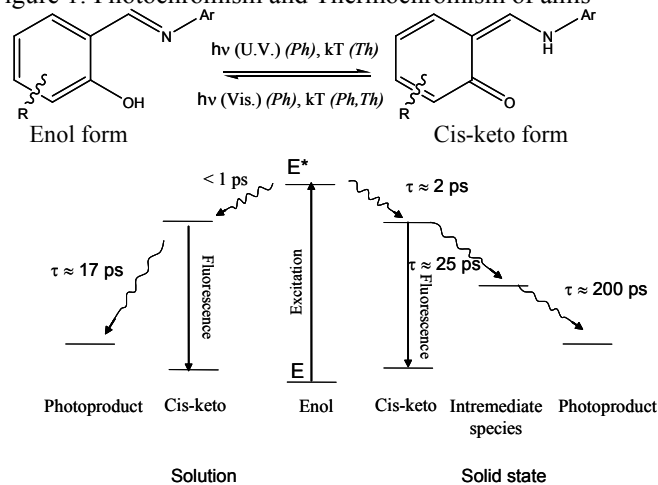


Figure 3: Dynamics of Photochromic reaction of 4-P in solution and in microcrystalline powder.

¹ M. Z. Zgierski and A. Grabowska, "Photochromism of salicylideneaniline (SA). How the photochromic transient is created: A theoretical approach", J. Chem. Phys., **2000**, *112*, 6329-6337