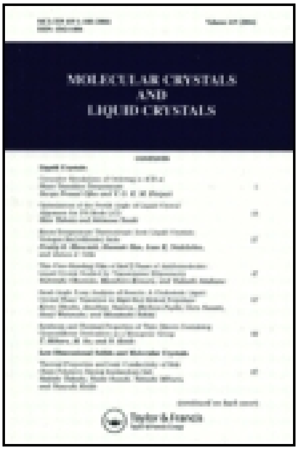

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Photochromic Dynamics of Salicylidene Aniline in Solid State by Using Femtosecond Transient Absorption Spectroscopy

T. Asahi [a] , H. Masuhara [a] , K. Nakatani [b] & M. Sliwa [c]

[a] Department of Applied Physics, Handai Frontier Research Center, Osaka University, Suita, Japan

[b] ENS Cachan - PPSM UMR, Cachan, France

[c] Department of Applied Physics, Handai Frontier Research Center, Osaka University, Suita, Japan, Japan and ENS Cachan - PPSM UMR, Cachan, France

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T. Asahi
H. Masuhara
Department of Applied Physics, Handai Frontier Research Center,
Osaka University, Suita, Japan

K. Nakatani
ENS Cachan – PPSM UMR, Cachan, France

M. Sliwa
Department of Applied Physics, Handai Frontier Research Center,
Osaka University, Suita, Japan and ENS Cachan – PPSM UMR,
Cachan, France

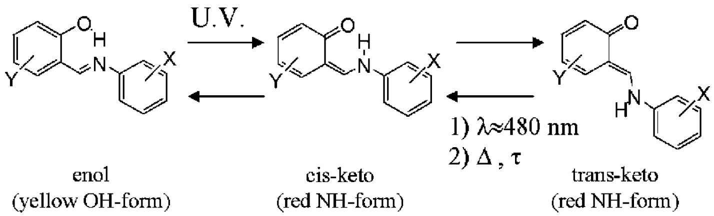
This paper reports the dynamics of the photochromic reaction of crystalline N-(3,5-di-tert-butylsalicyliden)-4-aminopyridine which can be applied for nonlinear optical photoswitches. The transient absorption spectra of the microcrystalline powder were measured by femtosecond diffuse reflectance spectroscopy and compared with those in ethanol solution. Similar photochromic reaction occurs in solid state and in solution, however some intermediate species were observed before the long lived photoproduct in solid state probably due to steric hindrance in the crystalline state.

Keywords: excited state dynamics; nonlinear optics; organic crystal; photochromic reaction; salicylidene aniline; second harmonic generation; time-resolved diffuse reflectance spectroscopy

INTRODUCTION

Molecular systems having photochromic behaviour are the target of considerable interest in applications such as optical data processing

Address correspondence to T. Asahi, Department of Applied Physics, Handai Frontier Research Center, Osaka University, Suita, 565-0871, Japan. E-mail: asahi@ap.eng.osaka-u.ac.jp



SCHEME 1 Photochromic reaction of salicylidene anilines.

and storage. Andes and Manikowski studied the photochromism characteristics of a crystalline salicylidene aniline from the point of view of data storage application; the crystal showed excellent fatigue resistance about 50 000 cycles alternating UV and visible light irradiation [1]. In salicylidene anilines and related Schiff bases, the photochromism is based on photo-induced proton transfer of the thermally stable enol form and the following isomerization to the metastable *trans*-keto one (Scheme 1) [2]. Back reaction occurs in dark or by irradiation with visible light. This isomerization can be applied to photo-switchable nonlinear optical properties, and the photoswitching of second harmonic generation (SHG) has been demonstrated for a polycrystalline film of N-salicylidene-4-bromoaniline (4-Br) [3]. Its SHG intensity can be reversibly modulated by a cyclic irradiation of UV and visible light, related to the photochromic reaction.

Recently, we have found that crystalline N-(3,5-di-tert-butylsalicyliden)-4-aminopyridine (4-P) (Fig. 1) is also photochromic and SHG active. Especially 4-P is interesting because it presents a slow back reaction of keto form; 125 days in crystalline phase, so that it can be used as a SHG photocommuter [4]. To reveal excited state dynamics of this solid and to consider the photoswitching mechanism, in this present work, we examined the transient absorption spectra and their temporal profiles for 4-P microcrystalline powder.

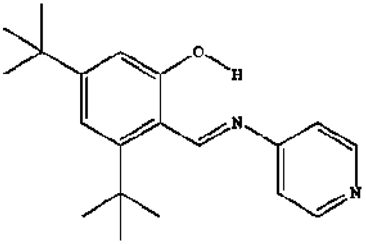


FIGURE 1 N-(3,5-Di-tert-butylsalicylidene)-4-aminopyridine.

Although femtosecond and nanosecond transient absorption measurements were reported for salicylidene anilines in solution [5–7], the photoproduct and its formation process has been still unknown. Tamai et al. made the hypothesis of the formation of some "metastable" twisted species state within a few hundred of femtoseconds in the ground state energy surface of the final *trans* photoproduct [7]. Photoreaction is expected to be slowed down in the solid state, and this would allow us to get detailed answer on the mechanistic issues of the photochromic reaction. In this paper, dynamics of the photochromic reaction of 4-P in powder sample using a femtosecond diffuse reflectance spectroscopy set-up is reported, and compared to the dynamics in solution.

EXPERIMENTAL SECTION

The set-up of our time-resolved diffuse reflectance spectroscopic system with an amplified Ti:sapphire laser system was previously described [8,9]. Transient absorption was presented by, $\%\,absorption = 100 \times (1 - R/R_0)$ where R and R_0 are intensity of diffuse reflected light of a probe pulse (a femtosecond white-light continuum) with and without excitation, respectively. The excitation laser pulse was a second harmonic (390 nm) of an amplified femtosecond laser pulse (780 nm, $3\sim4$ mJ/pulse, 170 fs, 10 Hz). The temporal resolution of transient absorption measurements with this spectroscopic system is less than 1 ps for organic microcrystalline powder. We measured the spectral data with a single shot of pulse excitation, changing the sample position every time. We adjusted the excitation intensity and condition to give a linear relation between % absorption and the concentration of absorbing species. The transient absorption spectra in ethanol were measured in a flow cell with 2 mm optical path length using a conventional transmittance-mode spectroscopy [10].

4-P was synthesized by the condensation of equimolar amounts of 3-5-di-tert-butylsalicylaldehyde and 4-aminopyridine; the reaction was performed by dissolving amine in the liquid aldehyde at 140°C for 2 h [4]. After purification by recrystallization in diethylether, purity of the product was checked by its melting point and NMR spectrum.

To obtain the steady state absorption spectra, sample powder was diluted with dry NaCl powder. The diffuse reflectance spectra were measured with a fluorometer (F-4500, Hitachi), using dry MgO powder as a reference. The absorption spectra were evaluated by using Kubelka-Munk function [11]. All measurements were performed at room temperature.

RESULTS AND DISCUSSION

Steady State Absorption Spectra

Figure 2 presents the absorption spectra of the microcrystalline powder of 4-P before and after irradiation with a UV light at 390 nm. To be sure that there is no keto form initially, the sample was irradiated with 520 nm light for a few minutes before measurement. The photoproduct has an absorption band covering the 425–575 nm range, centered at 480 nm. Because thermal back reaction of the photoproduct in solution is fast (a few ms), the absorption spectra were measured by nanosecond flash photolysis [4]. As shown in Figure 2, the absorption spectra of the powder sample and in ethanol solution are alike.

Femtosecond Transient Absorption in Solution

Transient absorption spectra of 4-P in ethanol (10^{-3} M) after excitation with a femtosecond 390 nm laser pulse (10 mJ/cm^2) are shown in Figure 3a. We observed the same spectral and time-dependent characteristics as analogous compounds in solutions [6,7,12,13]. After the rise of a broad band with a maximum around 450 nm which originates from the $S_n \leftarrow S_1$ absorption of the enol-form, three broad bands grow up in less than 1 ps: two bands at 435 and 520 nm are due to the excited state of *cis*-keto form (*cis*-keto*) after proton transfer of the excited enol form (E*), and a broad negative band with a minimum around 680 nm which can be assigned to the stimulated emission of

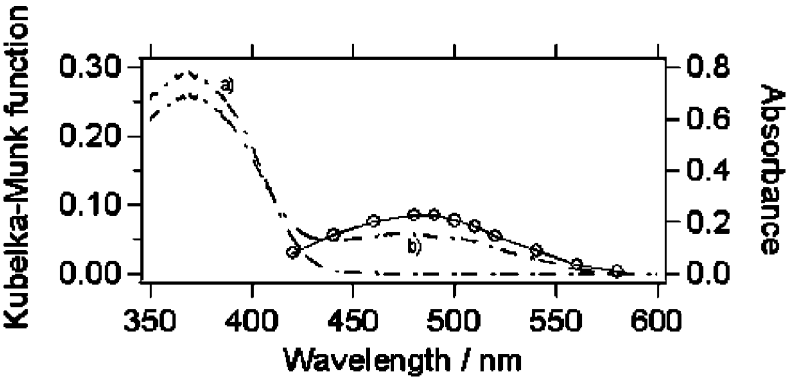


FIGURE 2 Dashed lines; absorption spectra (Kubelka-Munk function) of microcrystalline powder in NaCl (0.1 wt%) for 4-P (a) before irradiation (b) after UV irradiation. Solid line with circle; absorption spectrum of the photoproduct in ethanol (10^{-4} M).

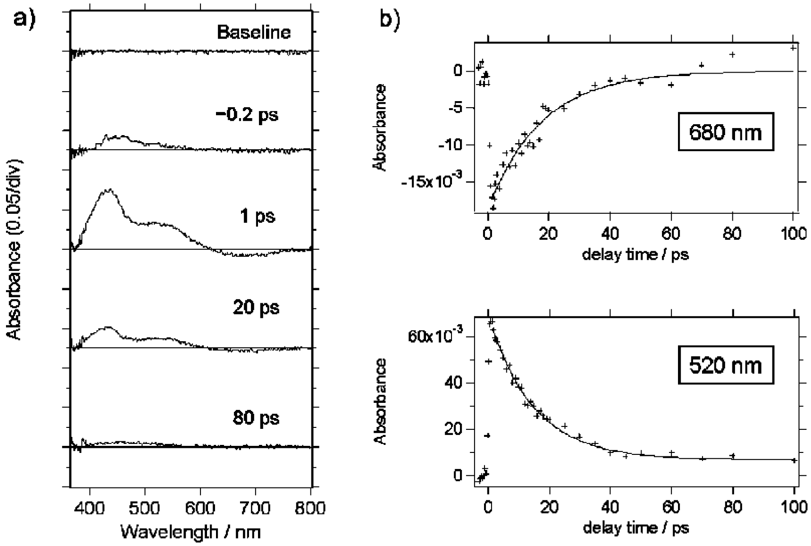


FIGURE 3 (a) Transient absorption spectra and (b) temporal profiles of transient absorption at 520 nm and 680 nm of 4-P in ethanol (10^{-3} M) with a 390 nm femtosecond laser pulse (10 mJ/cm^2).

the *cis*-keto*. All these bands show a single-exponential decay with the same lifetime of 17 ps (Fig. 3b and Table 1). Finally, a weak and broad absorption band attributed to the photoproduct remains, which is identical to the spectrum obtained by nanosecond flash photolysis.

The rise time of the transient absorption and induced emission of the *cis*-keto* was faster than the temporal resolution of our laser spectroscopic system. Consequently, it can be concluded that the proton transfer and the following relaxation in the excited state occur in less than 500 fs after excitation. The decay times of the transient absorption bands at different wavelengths are all equal (Table 1), so in the same time scale, *cis*-keto* relaxes both to its ground state and to the final photoproduct (photocoloured species).

TABLE 1 Absorption Maxima and Relaxation of Absorption Band in Crystalline Phase and in Solution

λ/nm solution	τ_1/ps	λ/nm solid state	τ_1/ps	τ_2/ps	τ_3/ps
435 nm	16.5	445 nm	2	25	190
520 nm	15.0	550 nm	2	25	200
680 nm	17.0	700 nm		25	

Femtosecond Transient Absorption in Solid State

Figure 4a presents the transient absorption spectra for 4-P powder after excitation with a femtosecond 390 nm laser pulse (3 mJ/cm^2). At 4 ps after excitation, the spectrum has two broad bands with maximum at 445 and 550 nm and one negative band around 700 nm due to a stimulated emission. This spectrum is similar to the transient absorption spectrum of the *cis*-keto* in ethanol, although slightly red shifted (see Table 1). Moreover, the relative intensities of the 445 and 550 nm bands are reversed compared to the spectrum in solution. This difference can be ascribed to the effect of the ground state absorption, since powder sample has an absorption tail up to 470 nm. From these considerations, we conclude that *cis*-keto* in solid state is generated at a few ps after excitation.

Figure 4b shows the temporal profiles of transient absorption at 550 nm and 700 nm. The decay at 550 nm was appropriately represented by a three-exponential decay with lifetimes of 2, 25 and 200 ps. The recovery of the negative signal at 700 nm due to the stimulated emission of *cis*-keto* can be fitted by a single-exponential with a lifetime of about 25 ps (Table 1). So we can consider the second component of 25 ps in the decay at 550 nm corresponds to *cis*-keto* in

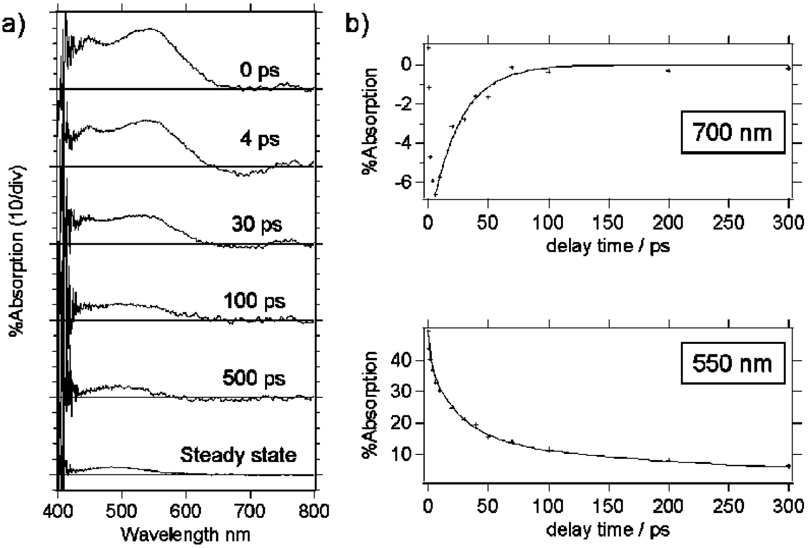


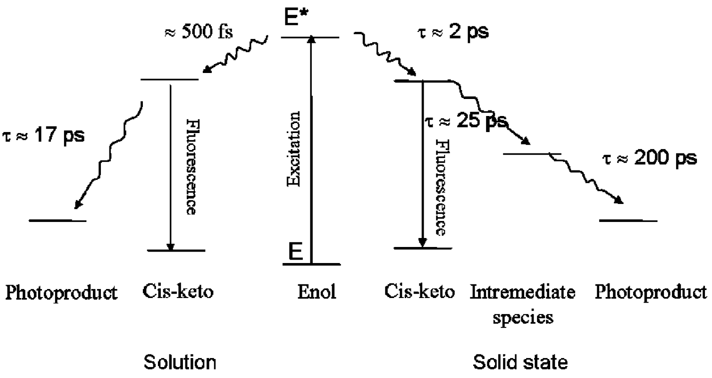
FIGURE 4 (a) Transient absorption spectra and (b) temporal profiles of transient absorption at 550 nm and 700 nm of 4-P powder with a 390 nm femtosecond laser pulse (3 mJ/cm^2).

solution. After the decay of cis-keto* (second component, 25 ps), a broad absorption band with a maximum at 500 nm remained. This band gradually shifts to the absorption band of the final photoproduct with a maximum at 480 nm in about 1 ns, the same band as obtained by the stationary study. As expected from previous studies [7,14], we have observed here an intermediate species before the long-lived photocoloured form.

A decay component of 2 ps lifetime was observed in the solid at wavelengths from 400 to 600 nm. Also, no negative peak around 700 nm was detected just after excitation. Therefore, the rapid decay can be ascribed to some relaxation process before the formation of fluorescent *cis*-keto*. Different hypothesis can be made for the origin of the new absorption band from 400 to 600 nm; the excited enol-form and a higher excited state of the *cis*-keto*, while more detailed study is necessary to make a conclusion.

CONCLUSION

A simplified scheme for solid state reaction, based on the above results and discussion is proposed (Scheme 2). First stage after photoexcitation is the proton transfer and the following relaxation to *cis*-keto*. The time scale in solid state (2 ps) is comparable to that in solution (a few 100 fs). Second one is relaxation of *cis*-keto* which is almost same in solid (25 ps) and in solution (17 ps). Formation of the final photoproduct (200 ps), on the other hand is slower compared to in solution (17 ps). This will be due to the lower free volume in crystalline state compared to solution, and the resulting the hindrance of the



SCHEME 2 Dynamics of the photochromic reaction of 4-P in solution and in microcrystalline powder.

cis-trans rotation. Some intermediate twisted species could be observed before the formation of the photoproduct.

As mentioned in the introduction, this study was aimed to analyze the suitability and the performance of 4-P as SHG photoswitch. Supposing that SHG modulation occurs between the enol state and the photoproduct, we demonstrated that this SHG switching may occur in 200 ps, since the photoreaction occurs at this time scale. So it justifies that 4-P would be a good candidate for ultrafast SHG photoswitching, and transient SHG studies should be the next step.

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