Why is Indigo Photostable over Extremely Long Periods?

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This experimental work clarifies the mechanism for the ultra-photostability of indigo carmine by direct observation of a transition state using a sub 5-fs laser pulse. The molecular structural changes during the photoexcited proton-transfer process were traced as the time-dependent instantaneous frequency of molecular vibrations. The mono-alcohol intermediate generated by proton transfer via stepwise path was found to be unstable, and it immediately reverted to indigo carmine. This regression to the reactant is the reason for the ultraphotostability of indigo over extremely long periods.

Indigo and indigo carmine are broadly used for dying because of their outstanding photostabilitiy, resulting in the persistence without any decoloration[1] even under light exposure. Another reason for their broad usage is that these dyes are strongly absorbed on cellulose and other fibers. In contrast, several other indigo derivatives have relatively high efficiencies of photoisomerization (Figure 1)[2] resulting in discoloration. Two mechanisms have been proposed for this difference in reactivity.[3] One possible mechanism is an ultrafast intramolecular proton-transfer reaction in the excited state, which is expected to be much faster than photoisomerization. The other is stabilization of the excited molecule by hydrogen bonding, which was proposed because of lack of direct experimental evidence of proton transfer. The question of whether or not a proton-transfer reaction of indigo and indigo carmine takes place has been a subject of controversial arguments for a long time[3] due to the absence of convincing evidence. In this paper, we report the identification of the transition state in the photoexcited proton-transfer process of indigo carmine by real-time observation of frequency changes using a sub 5-fs laser pulse.[4] This study experimentally clarifies the mechanism for the ultraphotostability of indigo and indigo carmine.

For direct observation of the electronic and vibrational dynamics after photoexcitation, a sub 5-fs pump–probe measurement was performed.[5] As a typical example of molecular vibrations, carbonyl stretching or C–C double bond stretching has a vibration period of about 20 fs. Therefore, molecular vibration can be real-time resolved using a sub 5-fs pulse. Therefore, if we use this sub 5-fs pulse, the molecular structural changes during the chemical reaction including the transition state can be traced as the changes in the instantaneous frequency of molecular vibrations.

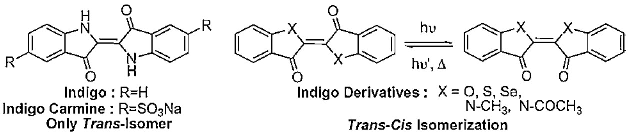

Figure 1. Left: Molecular structures of indigo and indigo carmine. Right: Molecular structures of indigo derivatives and schematics of photoisomerization.

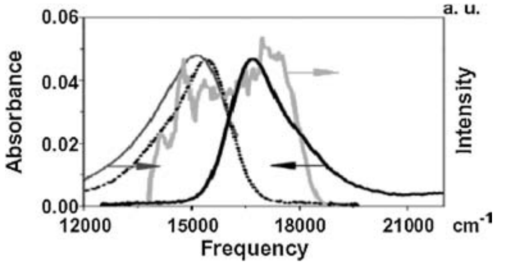

Figure 2. Absorption spectrum of indigo carmine (black), fluorescence spectrum of indigo carmine at 600 nm excitation (thin gray), its mirror image (black dots) with respect to the wavelength of the crossing point of normalized absorption and fluorescence spectra, and laser spectrum (light gray).

Saturated indigo carmine in anhydrous methanol in a 1-mm cell was used as a sample. Methanol was used as a solvent, because it has no molecular vibration signal in the vibrational frequency range examined. The absorption spectrum of the sample has a peak around 598 nm (black line in Figure 2) and the fluorescence spectrum of the sample at 600-nm excitation has a peak wavelength around 650 nm (thin gray line in Figure 2). The structure in the excited state is thought to be flexible because the fluorescence quantum yield is very low (0.0015)[1b] and the fluorescence spectrum is substantially red shifted by 500 cm^{-1} from the mirror image of UV absorption (dotted line in Figure 2). The spectrum of the sub 5-fs laser pulse extends from 525 to 725 nm (light gray line in Figure 2). Therefore, the absorption spectrum of indigo carmine overlaps with the laser spectrum, and indigo carmine is excited efficiently.

Figure 3a shows the real-time traces of absorbance change (ΔA, which was calculated as $\Delta A = -\log_{10}(1 + \Delta T/T)$ where T and ΔT are transmittance and transmittance change induced by the pump, respectively) for 128 probe wavelengths at room temperature (294 ± 1 K). The negative ΔA in the spectral range <705 nm is due to bleaching of the ground-state absorption and stimulated emission of indigo carmine, and positive ΔA in the range >705 nm is due to the induced absorption from the lowest excited singlet state ($S_n \leftarrow S_1$ transition).

Figure 3b shows a spectrogram[6] obtained by applying a sliding-window Fourier transform. Using a Blackman window function with a full width at half maximum (FWHM) of 120 fs, the spectrogram was calculated from real-time traces probed around

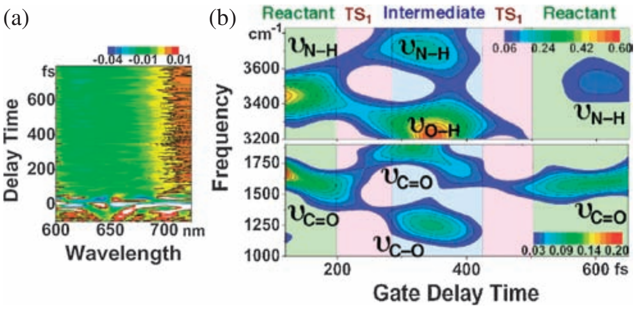

Figure 3. (a) A 2-dimensional display of absorbance change on the probe delay time and wavelength. (b) Spectrogram at 720 nm.

720 nm, where the positive ΔA has a maximum value. The frequency resolution of the spectrogram is $\pm 30\,\mathrm{cm}^{-1}$. The signal near 0-fs delay time could not be analyzed by the spectrogram of real-time modulated signal of electronic transition probabilities by molecular vibration due to the strong interference between the scattered pump and probe pulses. Spectrograms calculated in the spectral range where ΔA is positive are all similar in the distribution of the Fourier power.[5] Moreover, reproducibility of the signal was confirmed by repeating the experiment.

Initially after the photoexcitation, stretching modes of the two identical carbonyl groups ($\nu_{\mathrm{C=O}}$) of the reactant give rise to the peak centered around $1700\,\mathrm{cm}^{-1}$, in good agreement with the Raman frequency[7] independently measured in the present study.

This peak splits into two with red- and blue-shift at the gate delay time from 200 to 270 fs. The reason for this frequency shift can be explained as follows. After photoexcitation, the electron density in one of the two carbonyl bonds, which is the accepter of the transferred proton in the first proton transfer, decreases by π-electron delocalization extending to the transferred proton. The decrease in the electron density leads to the red-shift of $\nu_{\mathrm{C=O}}$. On the other hand, the electron density in the carbonyl bond that does not participate in the proton transfer increases by disappearance of hydrogen bonding between N–**H** and C=**O**. The increase of the electron density leads to the blue-shift of $\nu_{\mathrm{C=O}}$.

After 270 fs, a new peak around $1250\,\mathrm{cm}^{-1}$ appeared, which was attributed to a C–O single bond stretch ($\nu_{\mathrm{C\text{–}O}}$). The frequency of the mode was reported to be $1260\,\mathrm{cm}^{-1}$ in phenol.[8] The presence of this peak indicates that the C–OH is formed by the generation of mono-alcohol intermediate. This result gives direct evidence of the photoexcited proton transfer.

After the generation of the mono-alcohol intermediate, the peak around $1700\,\mathrm{cm}^{-1}$, which is considered to be due to a carbonyl stretch, is reproduced in the gate time range >500 fs.[9] This reappearance indicates that the back-reaction from the mono-alcohol intermediate to the parent indigo carmine. The first PT triggers the reaction from reactant to intermediate with high efficiency of >90%, estimated from the level of error and noise in the spectrogram, but the generated intermediate returns to indigo carmine within 0.5 ps also with high efficiency (>90%) resulting in the excellent stability without discoloration, providing a final answer as to whether or not proton transfer occurs in indigo carmine.[3]

A peak around $3450\,\mathrm{cm}^{-1}$ appeared just after photoexcitation and was assigned to a N–H stretch ($\nu_{\mathrm{N\text{–}H}}$). The frequency of this peak exhibits a gradual red shift and another peak around $3200\,\mathrm{cm}^{-1}$ appears at about 270 fs. The peak at $3200\,\mathrm{cm}^{-1}$ can reasonably be attributed to a O–H stretch ($\nu_{\mathrm{O\text{–}H}}$) because the new peak appears almost at the same time as that of $\nu_{\mathrm{C\text{–}O}}$. The red-shift is considered to be due to proton transfer in the generation of the mono-alcohol (i.e., the change from N–H to O–H), which has a lower vibrational frequency by about $(14/16)^{1/2}$ than $3450\,\mathrm{cm}^{-1}$. On the other hand, the electron density in the other N–H bond, which does not participate in the first proton transfer, is increased, leading to a blue shift of the peak because hydrogen bonding is weakened during the first proton transfer. When the formation of the mono-alcohol is completed, the peak around $3450\,\mathrm{cm}^{-1}$ ($\nu_{\mathrm{N\text{–}H}}$) reappears, as shown at the later delay time (>500 fs). These results are completely consistent with those for the carbonyl group dynamics.

The above results clearly provide direct evidence that proton transfer takes place after photoexcitation in indigo carmine, and show that the proton-transfer mechanism is a stepwise pathway.[10] We also obtained direct evidence indicating that even though the proton transfer takes place but the back reaction takes place to the original parent molecule with time constant of about 0.5 ps endowing the stability.

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