Photoisomerization of Symmetric Carbocyanines

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The phoisomerization process of symmetric carbocyanine dyes such as 3,3'-diethyloxadicarbocyanine iodide (DODCI), 3,3'-diethylthiadicarbocyanine iodide (DTDCI), 1,1'-diethyl-2,2'-dicarbocyanine iodide (DDI), 1,1'-diethyl-2,2'-carbocyanine iodide (DCI), and cryptocyanine (1,1'-diethyl-4,4'-carbocyanine) iodide (CCI) have been studied by measuring the steady state and time resolved fluorescence spectra and the ground-state recovery profiles. The steady-state fluorescence spectrum of photoisomer as a function of concentration and excitation wavelength provides the evidence that the fluorescence of photoisomer is formed by the radiative energy transfer from the normal form and the quantum yield for the formation of photoisomer is increased by decreasing the excitation wavelength. The fluorescence decay profiles have been measured by using the time correlated single photon counting (TCSPC) technique, showing a strong dependence on the concentration and the detection wavelength, which is due to the formation of excited photoisomers produced either by the radiative energy transfer from the normal form or by absorbing the 590 nm laser pulse. We first report the fluorescence decay time of photoisomers for these cyanine dyes. The experimental results are explained by introducing the semiempirical calculations. The ground state recovery profiles of DTDCI, DDI, and CCI normal forms have been measured, showing that the recovery time from the singlet excited state is similar with the fluorescence decay time.

Introduction

The cyanines are a class of molecules used for a wide range of applications, related to their characteristics to change the shapes upon the absorption of light. Cyanines have been used as the photo-sensitizer of silver halide particles,[1] the mode-locking dye in passively mode-locked laser,[2] the optical probes in membranes or model membrane systems,[3] and the initiators in photo-polymerization.[4] They show a very strong $\pi \rightarrow \pi^*$ absorption having a radiative lifetime of a few nanoseconds, and therefore the relaxation processes effectively competing with fluorescence emission should be fast. In solution, cyanine dyes, with no bulky substituent in the polymethine chain, adopt an all-*trans* configuration.[5-15] The photophysics of cyanine dyes have been extensively studied, and it is well established that following light absorption the dyes isomerize from the first excited singlet state to the ground-state photoisomer which has been proposed to have a mono cis conformation.[5-15] Deactivation processes of excited normal form take place in the pico- to nanosecond time scale, depending on the compound and the medium, whereas the back reaction of ground state photoisomer to the ground state normal form occurs in the micro- to millisecond. To some extent various applications of cyanine dyes depend on the details of the photoisomerization.

The questions central to understanding the photoisomerization of the cyanine are the identities of the photoisomer nature in solution. We will examine the photoisomerization process of a series of symmetric carbocyanines through the measurement of their radiative and nonradiative population relaxation kinetics. Since the cyanine molecules are used primarily in polar and/or viscous environments, we have chosen to study their behavior in the liquid phase using ethanol and ethylene glycol as solvents. These solvents exhibit extensive hydrogen bonding but different in the viscosites (1.078 *vs.* 26.09 cP). The energy relaxation pathways involving the intramolecular motion are usually influenced by the viscosity of solvent. We measured the steady-state and time resolved fluorescence spectra of the symmetric carbocyanine molecules differing in the polymethine chain length and/or the nature of the substitutent in the position 1 of indoline moiety. The cyanine dyes studied in this work are 3,3'-diethyloxadicarbocyanine iodide (DODCI), 3, 3'-diethylthiadicarbo-cyanine iodide (DTDCI), 1,1'-diethyl-2, 2'-dicarbocyanine iodide (DDI), 1,1'-diethyl-2,2'-carbocyanine iodide (DCI), and cryptocyanine (1,1'-diethyl-4,4'-carbocyanine) iodide (CCI). From the concentration and excitation wavelength dependence of the fluorescence spectrum, the lifetimes of excited photoisomer were estimated. The ground-state recovery profiles were measured by using the picosecond pump-probe laser technique. We performed the quantum Pariser-Parr-Pople molecular orbital (PPP MO) calculations to predict the absorption bands of the photoisomers.

Experimental

3,3'-Diethyloxadicarbocyanine iodide (DODCI, 98%), 3,3'-diethylthia- dicarbocyanine iodide (DTDCI, 98%), and 1,1'-diethyl-2,2'-carbocyanine iodide (DCI, 98%), cryptocyanine iodide (CCI, 98%) were purchased from Aldrich and used as received without further purification. 1,1'-Diethyl-2,2'-dicarbocyanine iodide (DDI, Exciton, 98%) was also used without purification. Ethanol (Aldrich, 99+%) and ethylene glycol (Merck, 99+%) are the spectrophotometric grade.

The steady-state fluorescence spectrum was measured by using a Aminco SLM 8000 spectrofluorometer. The fluorescence was observed from 90° to the center of a illuminated cuvette. The fluorescence measurement was also performed by using a triangular or a square cuvette oriented to

45° relative to the incident beam. The fluorescence decay was measured by using the time correlated single photon counting (TCSPC) technique. For all measurements, the polarization of excitation laser was rotated to 90° and checked the contributions of rotational diffusions to the signal. But, within our experimental uncertainty, we couldn't detect any difference in fluorescence decay profile for both polarization directions. The TCSPC technique is described only briefly here. The excitation laser is a mode-locked argon ion laser (Coherent Innova 200) pumping a dual jet dye laser (Coherent 700). The cavity-dumped dye laser beam with a Coherent 7220 Cavity Dumper has 2 ps pulse width and average power of 20 mW with Rh6G as a gain dye and DODCI as a saturable absorber at 3.8 MHz rate. The laser pulse was focused by using a 7-cm focal length lens and its intensity was adjusted to be below 10 W/cm^2 at the focused point. The emission signal was collected at 90° to the excitation laser beam by two 10-cm and 15-cm focal length lenses, focused onto a 20-cm monochromator (Jovin-Yvon H20), and detected with a photomultiplier tube (Hamamatsu model R2809). The signal was amplified by a wide band amplifier (Philip Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time to amplitude converter (Tennelec) and a counter (Ortec), and a multichannel analyzer(Tennelec/ Nucleus), and stored in a computer.

The apparatus used to measure the transient absorption spectrum with pump-probe technique is briefly described as follows. The laser source was a combination system of CW mode-locked Nd:YAG laser (Coherent Antares) pumping hybridly mode-locked synchronously pumped dye laser with group velocity dispersion (GVD) using four-prism pairs, a Nd:YAG regenerative amplifier (Continuum RGA60) and a three stage dye amplifier. The final laser pulses were 300-fs wide at 20 Hz, with an energy of 0.5 mJ/pulse at 590 nm. The sample was pumped by this laser pulse and probed by a continuous pulse generated by focusing the 590 nm laser pulse onto an 1-cm path length water cell. The probe pulse was passed through the sample cell, then focused onto a 30-cm monochromator, and finally detected by a photodiode array. The intensity change of probe pulse due to the absorption following the excitation was recorded as a function of delay time between pump and probe pulses. The signal was averaged for 200 laser shots, and then stored in a computer.

The electronic spectra of cyanine molecules were calculated by using SCF-CI method devolped by Paiser, Parr, and Pople, extended by an iterative variation of electronegativity of π atoms. All bonding and nonbonding interactions between the (atoms were calculated by means of Roothaan's formula for p-p overlap integral.

Results and Discussion

Steady-state fluorescence spectrum of carbocyanine dyes. Figure 1(A) shows the fluorescence spectrum of 10^{-3} M DTDCI in ethylene glycol (EG). The fluorescence spectrum of DTDCI/EG as a function of excitation wavelength was taken from the front face of a triangle cuvette oriented to 45° relative to the incident beam. As the excitation wavelength is decreased from 640 nm to 550 nm, total fluorescence intensity is reduced due to the decreased absorption and the fluorescence peak position is shifted from 685 nm to the longer wavelength. The inset of Figure 1(A) is the fluorescence spectrum taken from right angle to the illuminated face of a cuvette. It clearly shows that as the excitation wavelength decreases, the intensity of 720 nm band increases while that of 685 nm band decreases. The bands at 685 nm and 720 nm can be ascribed to the normal form and the photoisomer, respectively, which are consistent with the assignments by other workers.[8,11] Figure 1 and its inset indicate that the fluorescence of the photoisomer increases as the excitation wavelength decreases. Baumler and Penzkofer also reported that the population of DODCI ground-state photoisomer increases as the wavelength decreases, by measuring the temporal probe light absorption after pump laser switch-off.[9(b)]

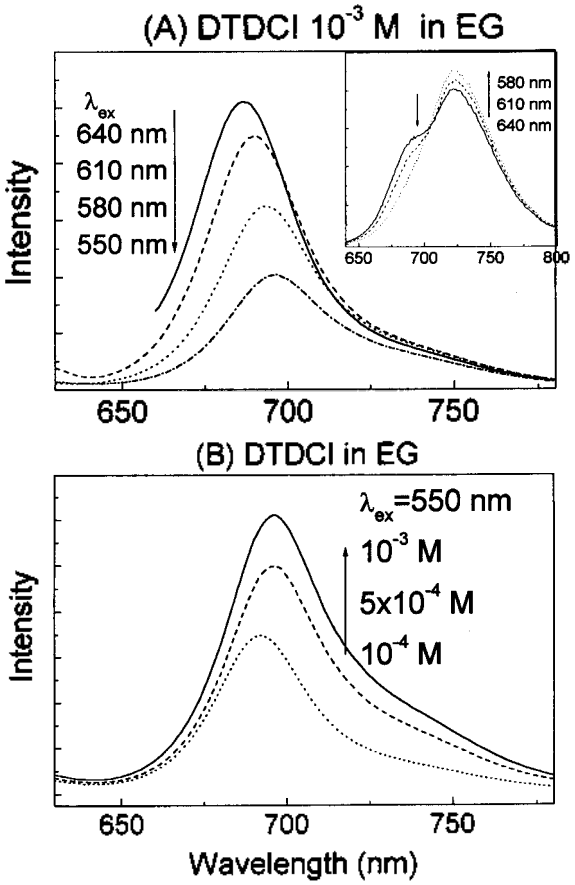


Figure 1. (a) The fluorescence spectrum of DTDCI 10^{-3} M/EG as a function of excitation wavelength. The fluorescence was taken from the front-face of a centrally illuminated cuvette. The inset shows the fluorescence spectrum of same sample which is taken from right angle to the incident beam using a square cuvette. (b) The fluorescence spectrum of DTDCI as a function of concentration. The excitation wavelength is 550 nm.

The fluorescence spectrum as a function of concentration, excited by 550 nm, is shown in Figure 1(B). The peak position is shifted to the longer wavelength with concentration, indicating that the photoisomer band is produced by the radiative energy transfer from the normal form, which is consistent with the suggestion for DODCI by Rulliére.[7]

The fluorescence spectra of DODCI, DDI, DCI, and CCI were measured as a function of excitation wavelength as

well as concentration, providing the peak position of the fluorescence band for the normal form and the photoisomer, as listed in Table 1. The steady-state fluorescence spectra of all these carbocyanines show that the fluorescence of photoisomer is produced by absorbing the fluorescence of the normal form, and the quantum yield for the photoisomer formation is increased as the carbocyanine dyes are excited to the more vibrationally excited state. The fluorescence peaks of photoisomer are coincident with the laser action wavelengths, showing that the formation of photoisomer plays an important role in lasing action.

Fluorescence decay time of normal form and photoisomer. Table 2 lists the fluorescence decay times of the carbocyanine dyes which are measured by TCSPC technique. The fluorescence decay profiles of DTDCI show a strong concentration dependence due to the fluorescence of photoisomer produced by radiative energy transfer from the normal form. The fluorescence decay time of normal form can be measured at low concentration where the fluorescence of photoisomer can be ignored. The fluorescence decay profiles were taken over the range of 630-740 nm. In 660-740 nm, the fluorescence decay profile at 5×10^{-7} M-10^{-6} M shows single exponential decay curve. The decay times are measured to be 1.30 ± 0.01 ns and 1.50 ± 0.01 ns, in EtOH and EG solutions, respectively, which can be ascribed to the normal form. The fluorescence lifetime of DTDCI in EtOH agrees well with a reported value, 1.28 ns. 16 We observed that as the concentration increases, the fluorescence decay time increases. Figure 2 shows TCSPC fluorescence decay profile of DTDCI/EG solution at 710 nm

Table 1. The peak wavelength of emission for the normal form and the photoisomer, and laser action wavelength of carbocyanine dyes

Dye	Emission Wavelength (nm)		
	Normal	Photoisomer	Laser[a]
DODCI	615	650	660
DTDCI	685	720	731
DDI	750	775	740-770
DCI	650	675	
CCI	730	745	

[a] ref. 23.

Table 2. The fluorescence decay time of normal form and photoisomer, and the transient recovery time of normal form

Dye		Fluorescence decay time (ps)		Ground state recovery (ps)
		Normal	Photoisomer	
DODCI	EtOH	1150 ± 10	≤1150	
	EG	1200 ± 10	2000 ± 100	
DTDCI	EtOH	1300 ± 10	1600 ± 100	1300 ± 200 (80%)
	EG	1500 ± 10	2100 ± 100	1500 ± 200 (70%)
DDI	EtOH	30 ± 5	≤30	45 ± 5
	EG	85 ± 5	≤85, 270 ± 20	75 ± 5
DCI	EtOH	<25	≤25	
	EG	63 ± 5	≤63	
CCI	EG	330 ± 5	≤330, 75 ± 5	400 ± 20

as a function of concentration. The fluorescence decay time is increased to 2.1 ± 0.2 ns at 10^{-3}-10^{-4} M. In EtOH, the decay time is increased to 1.6 ± 0.1 ns at the same condition.

Since DTDCI is excited by 590 nm, the fluorescence could be measured even at 630 nm where the absorption of normal form are overlapped. At the wavelength below 650 nm, the decay profile is fitted by a biexponential function with a new short decay time component. Figure 3 displays the fluorescence decay profile as a function of concentration at 650 nm, showing the biexponential decay curve with a constant short decay time, 300 ± 20 ps. Its contribution is $25\pm5\%$ over the concentration range 10^{-6}-10^{-3} M. The short decay time is also found to be 200 ± 20 ps in EtOH and its contribution is approximately 10% over the same concentration range. The contribution of this short decay time becomes about 50% at 630 nm. It is found that as the laser intensity is increased, the fluorescence profiles are also influenced. Therefore, the laser intensity is reduced until the decay profiles are unchanged. The average intensity of focused laser beam is adjusted to be ~10 mW/cm^2. Figure 4 shows the fluorescence decay behavior of 10^{-5} M DTDCI/EG as a function of detection wavelength, showing the double exponential function at 630-650 nm and the single ex-

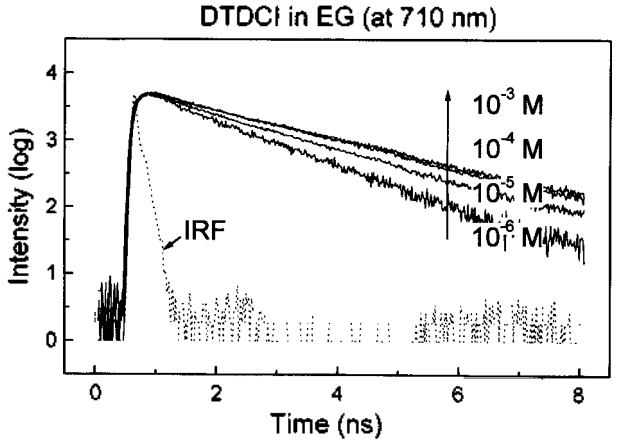


Figure 2. TCSPC spectrum of 10^{-3} M DTDCI/EG as a function of concentration at the detection wavelength of 710 nm. The excitation wavelength is 590 nm.

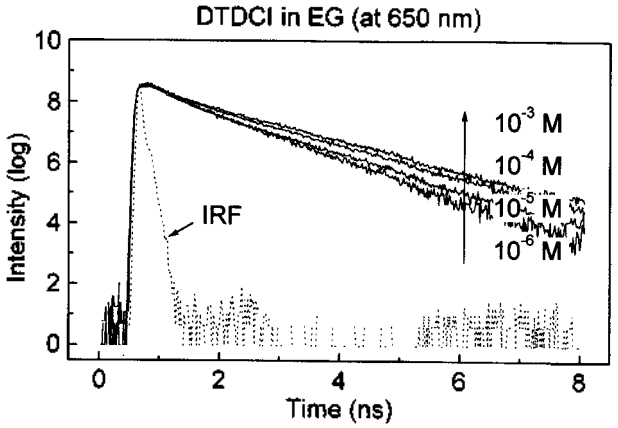


Figure 3. TCSPC spectrum of 10^{-3} M DTDCI/EG as a function of concentration at the detection wavelength 650 nm. The excitation wavelength is 590 nm.

ponential function at the wavelength longer than 680 nm.

Using TCSPC technique, the fluorescence decay time of DODCI normal form in EtOH is measured to be 1.15±0.01 ns at 10^{-6} M where the fluorescence of photoisomer is negligible. The photophysics of DODCI has been studied by a number of authors[5-13] and the fluorescence lifetime of the normal form in EtOH was reported to be 1.15 ns,[16,17] which is in good agreement with our value. The fluorescence decay time of DODCI in EG is measured as 1.20±0.01 ns at 10^{-6} M. The fluorescence decay time of DODCI in EtOH remains as the same even at the concentration of 10^{-3} M over the detection wavelength 605-680 nm. However, in EG, the decay time of fluorescence is increased to 2.0±0.1 ns as the concentration is increased to 10^{-3}-10^{-4} M.

The fluorescence decay profiles of 10^{-4} M DDI in EG solution, where the fluorescence of photoisomer in the steady-state fluorescence spectrum was found to be negligible, show the detection wavelength dependence; as the detection wavelength becomes shorter, the decay profile becomes biexponential due to a long decay component, as shown in Figure 5. At 720-760 nm the decay time is 85±5 ps, but at

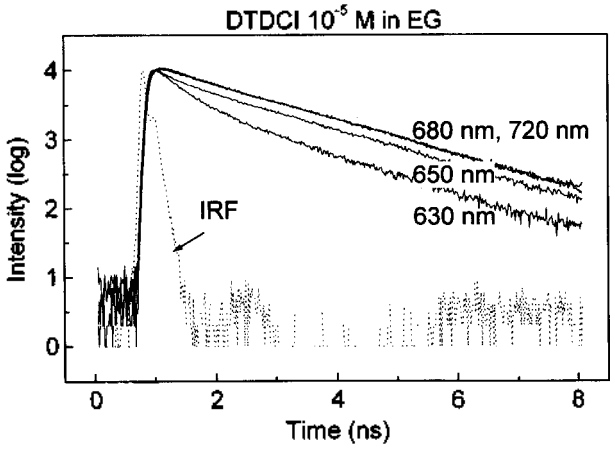


Figure 4. TCSPC spectrum of 10^{-5} M DTDCI/EG as a function of the detection wavelength. The excitation wavelength is 590 nm.

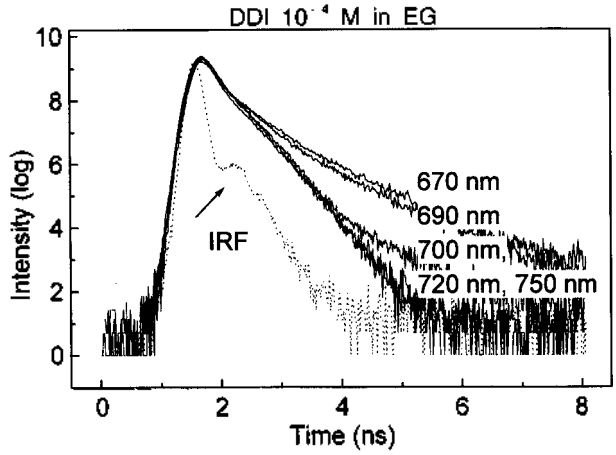


Figure 5. TCSPC spectrum of 10^{-4} M DDI/EG as a function of detection wavelength. The excitation wavelength is 590 nm.

670-720 nm the contribution of longer lifetime, 270±20 ps, is increased to ~10% as the detection wavelength is decreased to 670 nm. As the concentration is increased to 10^{-3} M, the decay profile still remains same. In EtOH, the fluorescence decay profile of DDI shows almost no detection wavelength and concentration dependence and the decay time is measured to be 30±5 ps.

The fluorescence decay profile of 10^{-3}-10^{-4} M CCI in EG were measured as a function of detection wavelength (670-760 nm), showing the dependence on the detection wavelength but not much on the concentration. The decay time is measured to be 330±5 ps at 730-760 nm, but the contribution of 75±5 ps is found to be increased to 50% at 670 nm.

The fluorescence decay time of DCI in EtOH is too short to be measured by using our system, but in EG the decay time has been measured to be 63±5 ps. The fluorescence decay profiles of DCI show almost no dependence on the detection wavelength and the concentration.

The high pulse repetition rate (3.8 MHz) of our picosecond laser system generates a steady-state mixture of normal form and photoisomers. Since the steady-state fluorescence spectrum measurement indicates that the fluorescence of photoisomer at the longer wavelength than the normal form is produced by radiative energy transfer from the normal form, only fluorescence decay times which are longer than that of the normal form can be measured. The decay times of photoisomer are 2.0±0.1 ns for DODCI/EG, 1.6±0.1 for DTDCI/EtOH, and 2.1±0.1 ns for DTDCI/EG, as listed in Table 2. The increase in solvent viscosity tends to increase the lifetimes of excited state by hindering nonradiative deactivation process. The dependence of fluorescence decay profile on the concentration must be due to change in the contribution of photoisomer fluorescence.

The DTDCI photoisomer which fluoresce at 660-720 nm has the longer decay time than the normal form. The short fluorescence decay time detected at the wavelength region 620-650 nm where the absorption of normal form are overlapped, suggests the existence of another photoisomer. Since this fluorescence shows the shorter decay time than the normal form, it should be produced either from the laser pulse excitation (590 nm) or the direct formation following the excitation of normal form. Then the decay time should be independent on the concentration, which can be found from the shorter lifetime component of Figure 4. The ground-state recovery profile measurement at 630-660 nm, described in the following section, shows that the direct formation of the excited photoisomer is not likely to take place. Therefore, the ground-state photoisomer which can absorb the 590 nm laser pulse produces the fluorescence at 630-650 nm. Our argument is consistent with the suggestion of Bilmes *et al.* who reported the absorption spectrum of DTDCI photoisomer overlapped with that of the normal form in the 600-680 nm region.[12] Sundtsröm *et al.* suggest that the photoisomer absorbs around 550 nm to be excited into the excited state having the lifetime 270±20 ps.[18]

In the case of DDI and CCI in EG solution, no concentration dependent fluorescence behavior at the longer wavelength region indicates that the fluorescence decay time of its photoisomer is shorter than or equal to that of the normal form. The lifetimes appeared at the shorter

wavelength region are due to the photoisomer which fluoresce by the absorption of 590 nm laser pulse (see the following section describing the ground-state recovery measurement of DDI and CCI).

Contrary to DODCI and DCI, three carbocyanines DTDCI, DDI, and CCI are excited to the vibrationally excited state by 590 nm laser pulse and thus the quantum yields of photoisomer is expected to be high. The produced ground-state photoisomers which can absorb the 590 nm laser pulse will produce the fluorescence at the wavelength region where the absorption band of the normal form is overlapped.

Awad *et al.* carried out semi-empirical calculations for the isomerization surfaces of the ground and excited states DODCI and DTDCI. The potential energies are calculated for the normal form having all *trans* geometry and its isomers which can be produced from sequential rotations around C-C bonds. The possible photoisomers of the symmetric cyanines produced from single-photon process have been discussed by Churio *et al.*[13] and Rofdriguez *et al.*,[20] who suggest that only three conformations of dicarbocyanine fulfill the condition that only one double bond is isomerized for the single-photon absorption. Rofdriguez *et al.* used the semiempirical calculations to show that, in the case of DODCI and DTDCI, the activation barrier for the rotation around the bond connecting the polymethine chain to the end oxaindoline moiety is much higher than that for the rotation around any of the two bonds located within C-C atoms of the polymethine chain, thus two photoisomers are expected to be obtained at most upon the single-photon excitation.

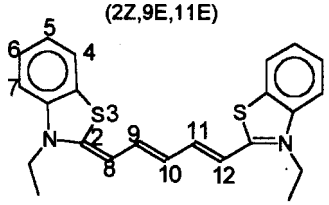
In our experimental conditions, all possible isomers can be produced to form the steady-state mixture of photoisomers. We carried out semiempirical PPP MO calculation to predict the absorption peak position of photoisomers relative to the normal form. Table 3 lists the calculated absorption peak positions of cyanines. For DODCI, the isomers which absorb the shorter wavelength than the normal form cannot be excited by 590 nm laser pulse. However, in the case of DTDCI and DDI, the isomers whose absorption peak is located at shorter wavelength than that of the normal form can absorb 590 nm laser pulse and give the fluorescence at the wavelength where the absorption band of the normal form exists. The isomers produced by the rotation around the bond connecting the polymethine chain to the end indoline moiety, should have higher activation barrier than the isomers formed *via* the rotation around any of the two bonds located within C-C atoms of the polymethine chain and show the longer relaxation time. In DDI, these isomers, *e.g.* (2E,10E,12Z), (2E, 10Z,12Z), have the shorter absorption peak than the normal form, which explains the experimental results of DDI/EG solution. For DCI, the absorption wavelengths of isomers are shorter than or similar to that of normal form. On the other hand, in the case of CCI, all photoisomers can absorb the 590 nm laser. The short decay time component in CCI/EG must be due to these isomers. It is suggested that there is no energy barrier in the excited state of the 1,1'-diethyl-4, 4'-cyanine iodide.[19] Therefore, if CCI has no energy barrier for the twisting the C-C bonds, the fluorescence decay time of photoisomer is expected to be shorter than the normal form.

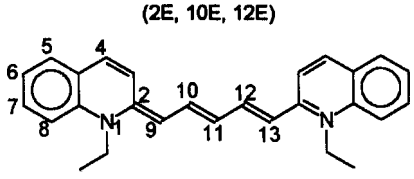
Ground state recovery and transient absorption measurements. The ground state recovery profiles are measured for DTDCI, DDI, and CCI which show two different fluorescence decay times. The ground state recovery profiles of DTDCI/EG have been measured at 630-690 nm. Figure 6(A) shows the ground state recovery profiles at 660 nm. The excitation wavelength is 590 nm, the concentration of DTDCI is 10^{-3} M, and the repetition rate of pump-probe lasers is 20 Hz. Under this low repetition rate, the amount of photoisomer accumulated in the cell can be negligible. The ground state recovery times at 660 nm are 300 ps and 1.5 ns as a ratio of 3 : 7. Over the scanning rage of 630-690 nm, the ground state recovery is measured to be approximately same. In EtOH, the recovery times are measured to be 200 ps : 1.3 ns as a ratio of 1 : 4. The recovery times 1.3 ns and 1.5 ns, respectively, in EtOH and EG,

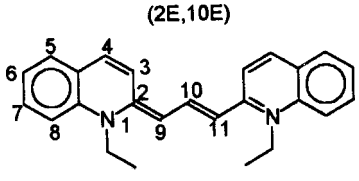
Table 3. The absorption peak wavelength of carbocyanine conformers calculated by PPP MO method

	(2Z,9E,11E)	(2Z,9E,11Z)	(2Z,9Z,11E)	(2E,9E,11E)	(2Z,9Z,11Z)	(2E,9E,11Z)	(2E,9Z,11E)	(2E,9Z,11Z)
DODCI	600[1]	608	624	576	620	579	581	639
DTDCI	655	670	681	619	681	690	700	623
	(2E,10E,12E)[2]	(2E,10E,12Z)	(2E,10Z,12E)	(2Z,10E,12E)	(2E,10Z,12Z)	(2Z,10E,12Z)	(2Z,10Z,12E)	(2Z,10Z,12Z)
DDI	700	636	722	705	644	707	731	729
	(2E,10E)[3]	(2Z,10E)	(2E,10Z)	(2Z,10Z)				
DCI	591	527	607	557				
	(4E,10E)	(4Z,10E)	(4E,10Z)	(4Z,10Z)				
CCI	696	624	684	690				

[1] DTDCI [2] DDI [3] DCI







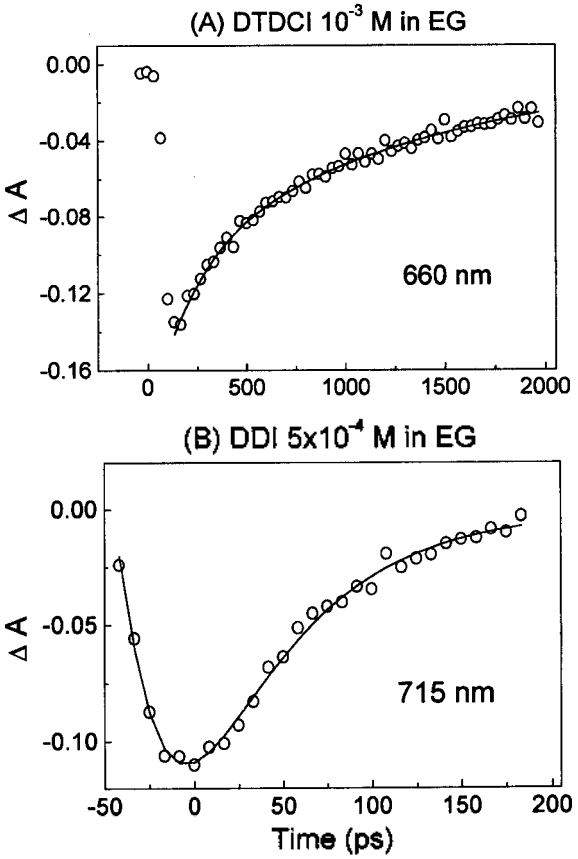


Figure 6. (A) The ground state recovery signal at 660 nm for 10^{-3} M DTDCI in EG at 660 nm. The curve represents the fitted double exponential function for data point (○). The recovery times are 300 ps and 1.5 ns with the relative ratio of 3 : 7. (B) The ground state recovery signal at 710 nm for 5×10^{-4} M DDI in EG at 660 nm. The curve represents the fitted single exponential function for the data points in recovery region (○). The recovery time is 75±5 ps.

agree well with the fluorescence decay times of normal form. There is no stimulated emission in the spectral regime of photoisomer fluorescence, 630-650 nm, indicating that the photoisomers are produced in the ground state.

In EG, the recovery profile is approximately fitted by single exponential function over the range of 690-760 nm and its recovery time is 75±5 ps, which is longer than that in EtOH, 45±5 ps.[22] The stimulated emission is also not found in 690-710 nm region. Figure 6(B) is the ground state recovery profile of 5×10^{-4} M DDI/EG at 710 nm. In the case of CCI, the recovery time is found to be 400± 20 ps. The recovery times of DDI and CCI are in good agreement with the fluorescence decay times of normal form.

The Rulliére developed a model for the ground- and excited state isomerization surfaces of DODCI,[7] the population relaxation kinetics can be modeled easily. The ground state, the excited state, and the twisted intermediate excited state are symbolized by S0, S1, and T. The population for S_0, S_1, and T are expressed by following equation.[21]

$$S_1(t) = S_1(0)\exp(-k_\Sigma t)$$

$$T(t) = \frac{S_1(0)k_{isom}}{k_T - k_\Sigma}\left[\exp(-k_\Sigma t) - \exp(-k_T t)\right]$$

$$S_0(t) = S_0(0) + s_1(0)\left\{\frac{k_T + k_{nr} + \varphi k_{isom}}{k_\Sigma} + \frac{\varphi k_{isom}}{k_T - k_\Sigma}\exp(-k_T t) + \frac{k_r + k_{nr} - \varphi k_T}{k_T - k_\Sigma}\exp(-k_\Sigma t)\right\}$$

Here, k_r is the radiative decay rate constant from S_1, k_{nr} is the nonradiative decay rate constant, k_{isom} is the rate constant for crossing the excited-state barrier, k_T is the decay rate constant for T, and φ is the branching ratio for decay of T to either of the possible isomeric ground-state structures. The equation was based on the assumption that there is insignificant population of the excited state isomer and the exchange between the ground-state isomers is negligible on the time scale of these relaxation processes. First assumption is valid when the normal form of cyanine is excited exclusively. The second assumption is also valid since the ground-state barriers for cyanine is high enough; for example, DODCI and DTDCI in EtOH have been measured to be 13.6 and 11.2 kcal/mol, respectively.[14,15] These equations predict that the fluorescence decays as a single exponential and the ground state population recovers as a double exponential with the contribution from both direct S_1 relaxation and relaxation through the twisted intermediate excited state.

According to this kinetic model for one conformer, the short and long decay times found in ground state recovery profiles of DTDCI correspond to the recovery times from the twisted intermediate and the singlet excited state, respectively. The decay time from the singlet excited state to the ground state is consistent with the fluorescence decay time of normal form. The short component in the ground state recovery profile is coincident with the fluorescence decay time of photoisomer observed at the wavelength 630-650 nm. Awad *et al.* measured the ground state recovery profiles of DTDCI by using picosecond laser with 82 MHz, showing the biexponential recovery profiles having 1.6 ns (53%) and 255 ps (47%).[21] Our results are very consistent with the result of Awad *et al.* In the case of CCI and DDI, the recovery time *via* intermediate might not be detected probably due to limit in time resolution or low signal intensity of our system.

Conclusion

The relaxation processes of symmetric carbocyanine dyes such as DODCI, DTDCI, DCI, DDI, and CCI have been studied by measuring the steady state and time resolved fluorescence spectra and the ground-state recovery profiles. The fluorescence spectrum of photoisomer has been measured as a function of concentration and excitation wavelength, providing the evidence that the fluorescence of photoisomer is formed by the radiative energy transfer from the normal form and the quantum yield for the formation of photoisomer is increased by decreasing the excitation wavelength. The fluorescence decay times have been measured by a function of concentration by using time correlated single

photon counting (TCSPC) technique. The fluorescence decay times of most these carbocyanine dyes are strongly dependent on the concentration and the detection wavelength, which is due to the formation of excited photoisomers produced either by the radiative energy transfer from the normal form or by 590 nm laser pulse. In DTDCI, DDI, and CCI, which can be excited to vibrationally singlet excited state by 590 nm, the fluorescence decay times of photoisomer excited by laser pulse were also found. The presence of these photoisomer is predicted by PPP-MO semiempirical calculations for the peak wavelengths. The ground state recovery profiles of DTDCI and DDI normal form were measured, showing that the recovery time from the singlet excited state is similar with the fluorescence decay time.

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