BULLETIN
OF THE
KOREAN CHEMICAL SOCIETY

VOLUME 15, NUMBER 6
JUNE 20, 1994

BKCS 15(6) 413-516
ISSN 0253-2964

Communications

Picosecond Spectroscopic Studies on Monomer and Dimer of the Mode-Locking Dye, 1,1′-Diethyl-2,2′-dicarbocyanine Iodide (DDI)

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Received November 9, 1993

The cyanine dye 1,1′-diethyl-2,2′-dicarbocyanine iodide (DDI) has been widely employed as Q-switching[1] and mode-locking dyes in ruby laser system.[2] Spaeth and Sooy,[3] using ruby laser excitation technique, observed that DDI in methanol exhibits two fluorescence lifetimes: $\tau_1<3$ ns and $\tau_2>25$ ns. Duguay and Hansen,[4] using an ultrafast Kerr cell and 532 nm picosecond laser excitation, measured the lifetime of 14± 3 ps for the S_1 state of DDI in methanol or acetone. Dempster *et al.*[5] estimated the fluorescence lifetime of DDI in ethanol to be 11.5± 2.5 ps based on the quantum efficiency at 600, 625, and 650 nm, $(2.8\pm 0.4)\times 10^{-3}$, and the calculated natural radiative lifetime, 4.1± 0.4 ns.

Cyanine molecules form aggregates in aqueous solution at high concentration and on surfaces. Aggregation occurs because of the strong dispersion forces associated with the high polarizability of the chromophoric chain. In aqueous solutions, the high dielectric constant of water facilitates the aggregation process by reducing the electrostatic repulsion between similarly charged dye molecules. These aggregates are ideal models for light-harvesting arrays in biological systems because the molecules are in a relatively well-defined structure.[6] However, since the relaxation process takes place in picosecond time scale, there have been few studies on the dynamics of DDI aggregates. Recently, Chen *et al.*[7] obtained the non-exponential picosecond bleaching signal in the ground state absorption profile of DDI aggregates formed in colloidal solution, showing the average recovery time as 120-130 ps and a strong anisotropy.

We used the picosecond laser spectroscopic techiques to investigate the photophysical properties of DDI. Our objective of this study is to unravel the effect of dimer concentration on the energy relaxation of monomer as well as the size effect on the lifetime of photoexited aggregates. We focus on measuring the lifetime of DDI monomer using picosecond fluorescence, transient bleaching, and transient absorption spectra.

Time-correlated single photon counting (TCSPC) system has been described in detail elsewhere,[8] and only a brief description is given here. The excitation laser is a picosecond dual jet dye laser (Coherent 700) pumped by a mode-locked argon ion laser (Coherent Innova 200). The cavity dumped beam from the dye laser with Coherent 7220 Cavity Dumper has 2 ps pulse width and average power of 50 mW at 3.8 MHz reptition rate with Rh6G as gain dye and DODCI as a saturable absorber. The emission was collected at 90 degree angle to the excitation laser beam by 10 cm and 15 cm focal length lenses, focused onto a Jobin-Yvon H20 monochromator, and detected with a microchannel plate photomultiplier tube (Hamamatsu R2809U). The signal was amplified by a wideband amplifier (Phillips Scientific), sent to a Quad constant fraction discriminator (Tennelec), a time-to-amplitude converter (Tennelec), a photoncounter (Ortec), and a multichannel analyzer (Tennelec/Nucleus), and finally stored in a computer.

The apparatus to measure the transient absorption spectrum with pump-probe technique is briefly described as follows.[9] The laser system is a combination of cw mode-locked Nd : YAG laser (Coherent Antares) pumping hybridly mode-locked synchronously pumped dye laser with group velocity compensation using four prism sequence, Nd : YAG regenerative amplifier (Continuum RGA60) and 3 stage dye amplifier. The final pulses are 20 Hz, 300 fs, and 0.5 mJ/pulse at 590 nm. The sample in a 2 mm pathlength flowing cell was pumped by the laser pulse at 590 nm and probed by a continuum pulse generated by focusing the 590 nm laser pulse onto an 1 cm pathlength water cell. The probe pulse passed through a sample cell was focused onto a 30 cm monochromator and detected by a photodiode array. The signal was averaged for 200 laser shots, and stored in a computer. The probe intensity change due to the absorption following the

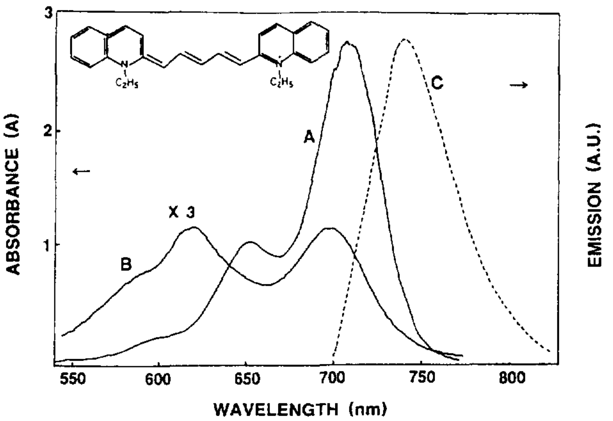

Figure 1. Absorption spectrum of 10^{-5} M DDI in ethanol (A) and 5×10^{-6} M DDI in water (B). Emission spectrum of DDI excited by 580 nm (C) is shown as dotted line.

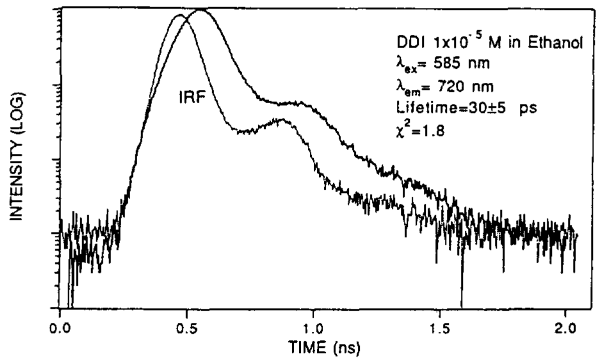

Figure 2. Fluorescence decay profile (at 720 nm) of 10^{-5} M DDI in ethanol, excited by 2 ps, 10 nJ/pulse, and 585 nm laser. Instrument response function (IRF) is shown in shorter time region. The FWHM of IRF is 40 ps. The single exponential fitting yields the lifetime of 30± 5 ps.

excitation was recorded as a function of delay time between pump and probe pulses.

DDI (Exciton) was used without further purification. Ethanol (Aldrich spectroscopic grade) and triply-distilled water were used as solvents.

The absorption and the corrected fluorescence spectra of DDI in ethanol and in water are shown in Figure 1. The absorption peak at 710 nm and the secondary absorption peak at 650 nm in the spectrum of DDI in ethanol are $0\leftarrow0$ and $1\leftarrow0$ vibronic transitions of the monomer, respectively. The band at 620 nm in the spectrum of aqueous DDI solution can be assigned to the dimer. Comparing the monomer and the dimer spectra in Figure 1, the following points should be emphasized.

(1) The peak-to-peak separation is $\sim$1300 cm^{-1} in the monomer indicating the familiar skeletal mode; in the dimer the separation is considered to be larger, namely 1840 cm^{-1}.

(2) The small shoulders at 590 nm in the monomer spectrum and at 570 nm in the dimer spectrum correspond to the third peak of the vibronic progression.

(3) The dependence of the absorption spectrum on the concentration of DDI in water is examined; as the concentration decreases, the dimer peak decreases.

Strong electronic coupling between cyanine dye molecules in these aggregates gives rise to an absorption band which is either blue shifted or red-shifted from the monomer band. For example, the aggregates of 1,1'-diethyl-2,2'-cyanine, or pseudoisocyanine exhibit a narrow absorption band, called the J-band, at $\sim$570 nm,[10] which is red-shifted from the monomer band at 523 nm, whereas the aggregates of carbocyanine dye and dicarbocyanine dye such as DDI exhibit a band, called the H-band, which is blue-shifted from the monomer band.[6,11] By use of one-dimensional exciton model,[11] the orientation of molecules in the aggregate can be inferred from the spectral shifts. In this model, the dye molecules are stacked as a tilted deck of cards and dipolar coupling is assumed. The interactions between these dyes at small intermolecular distance may not be well-approximated by dipole-dipole interactions, because the transition dipole moment in these dyes is spread over a large π-electron cloud. Nontheless, it is possible to obtain crude estimates of the molecular orientation in aggregates. In this model, spectral shifts are proportional to ($1-3\cos^2\theta$), where θ is the angle between the transition dipole moment of molecule in the aggregate and the long axis of the aggregate. Thus, the aggregate bands are blue-shifted for $54.44°<\theta<90°$ and red-shifted for $0<\theta<54.44°$.

Both samples exhibit the same fluorescence spectrum profile as shown as the dotted curve in Figure 1. The excitation wavelength was 585 nm and the fluorescence peak appeared at 760 nm for both sample, indicating that the dimer doesn't fluoresce. Fluorescence quantum yield of DDI in ethanol was determined to be $(2.8\pm0.4)\times10^{-3}$ by Dempster *et al.*[5] The one-dimensional exciton model[11] also predicts that J-aggregates will fluoresce very strongly, whereas H-aggregates will not fluoresce or will fluoresce very weakly. Therefore, the fluorescence of DDI dimer is not observed as expected from this model.

Time resolved fluorescence decay profile of DDI in ethanol, shown in Figure 2, is obtained at monitoring wavelength of 720 nm by TCSPC. The fitted decay time is 30± 5 ps with $\chi^2=1.8$, independent of the DDI concentrations. Figure 3(a) shows the transient bleaching spectra of 1×10^{-5} M DDI in ethanol as a function of delay time between the pump and probe laser pulses. The recovery time is found to be 40± 5 ps, which is fairly consistent with the value resulted from TCSPC. The fluorescence lifetime and the recovery time of transient absorption spectrum of monomer are longer than the previously reported values, 14± 3 ps obtained by Duguay and Hansen[4] or 11.5± 2.5 ps by Dempster *et al.*[5] It is possible that the 532 nm used by Dugay and Hansen excites the DDI with excess vibrational energy and yields the shorter lifetime or their few data points cause the error. Dempster *et al.* mesaured the fluorescence yield and then calculated the lifetime using the natural radiative lifetime from the expression of Forster.[5] The direct measurements of fluorescence lifetime as well as recovery time of ground state are probably more accurate than the calculated value based on a certain model expression.

Figure 3(b) shows the transient absorption spectra of 1×10^{-4} M DDI in ethanol as a function of delay time between the pump and probe pulses. The transient absorption signals grow from 0.3 ns to 2 ns following the pump laser pulse, indicating the formation of DDI triplet state. No significant

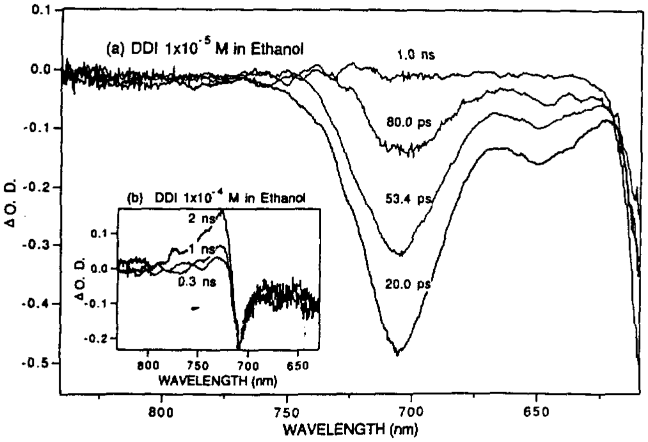

Figure 3. (a) Transient bleaching spectrum of 1×10^{-5} M DDI in ethanol. The recovery time is 40± 5 ps. The excitation wavelength is 585 nm. (b) Triplet-triplet absorption spectrum of 1×10^{-4} M DDI in ethanol. The transient absorption signals are built up from 0.3 ns to 2 ns following the pump laser pulse.

transient absorption signals were detected from 1×10^{-5} M solution due to the relatively weak triplet-triplet absorption at this concentration. Dempster *et al.*[5] reported broad triplet-triplet absorption spectra in the region of 450 to 627 nm and 740 to 810 nm by producing the DDI triplet state through the energy transfer from naphtalene. The transient absorption and depletion signals were observed to build up from zero to ~125 μs following the flash. The transient signal shown in Figure 3(b) is consistent with a portion of their spectra. The triplet-triplet absorption peak arising nearby 720 nm is pulled down by the strong bleaching peak at 710 nm so that the maximum build-up time is not clearly observed. More study is being undertaken to obtain the transient absorption spectrum of the excited singlet states as well as the triplet states.

The transient bleaching peak of aqueous DDI solution is also difficult to detect for the same reasons. Chen *et al.*[7] obtained an average transient bleaching lifetime of H aggregates of DDI on colloidal silica to be 120-130 ps, which is longer than the lifetime of monomer. Thus, the lifetime of cyanine dye is extremely sensitive to the rigidity of the local environment. This is partially attributed to the torsional dynamics of the polymethine chain. The singlet excited state lifetime of a molecule is given by $(k_r+k_{nr})^{-1}$, where k_r and k_{nr} are the radiative and the nonradiative rate constants, respectively. If the torsional relaxation along the polymethine chain affects the nonradiative rate, the inhibition of this motion decreases k_{nr} and consequently increases the lifetime of the singlet excited state. As we observed from the absorption spectrum, the skeletal mode frequency of dimer is higher than that of monomer. Therefore, the nonradiative relaxation rate due to this motion gets smaller in the dimer, which is consistent with the Chen *et al.*'s explanation for the lifetime of aggregates. The lifetime of the dimer is expected to be longer than 30 ps and shorter than 120-130 ps. We plan to study the photophysical properties of a series of cyanine dyes.

Time resolved fluorescence decay profiles of 1×10^{-5} M and 2.5×10^{-6} M DDI in water are also measured, representing the decay time of 18± 3 ps and 25± 5 ps with χ^2 less than 2, respectively. The fluorescence lifetime is slightly influenced by the DDI dimer concentrations. The fluorescence decay time of monomer decreases as the concentration increases. This result follows qualitatively Forster model,[12] which predicts that with increasing dimer concentration, the energy transfer efficiency increases and the lifetime of the excited monomer decreases. However, since the cyanine with a long alkyl chain such as DDI in aqueous solution is known to be very easily decomposed by oxidation of iodide in the presence of light or heating, it is difficult to make an accurate measurement of the lifetime for DDI aqueous solution at concentrations of 10^{-6} M and less. Furthermore, the fluorescence of DDI is too weak to be measured by TCSPC at such a low concentration. At the concentration of higher than 10^{-5} M, the lifetime is too short to be measured with our detection system. For these reasons, the experiments were undertaken only for narrow concentration range.

In summary, we analyzed the absorption and the fluorescence spectra of monomer and dimer of DDI. It is the first time to measure the fluorescence decay time as well as the transient bleaching recovery time of DDI monomer, which are 30± 5 ps and 40± 5 ps, respectively. The fluorescence decay time of the monomer decreases as the concentration of the dimer increases, which might be explained in terms of energy transfer to the dimer. The transient absorption spectrum of the triplet state is also reported.

Acknowledgement. This work has been supported by KOSEF to D. Kim through Center of Molecular Science. J. Park acknowledges contributions from D. W. Cho and O. K. Song, who measured the absorption and steady-state fluorescence spectra in this work.

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Electrochemical Reduction of Thionyl Chloride: Solvent Effects

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Received January 4, 1994

Studies on the electrochemical reduction of thionyl chloride in nonaqueous media have been reported by several groups of investigators[1-4]. Experiments were run in these studies to elucidate the reduction mechanism in nonaqueous solutions containing tetraalkylammonium salts as a supporting electrolyte. Studying reduction mechanisms involved in neat thionyl chloride is difficult or impossible owing to the passivation of the electrode surface by the LiCl precipitate formed during the reduction of thionyl chloride[5-9],

$$2SOCl_2 + 4e^- \longrightarrow S + SO_2 + 4Cl^-$$

As a result, a single broad reduction cyclic voltammetric (CV) peak is observed, and extremely low currents flow beyond this peak potential. Nonaqueous solvents and non-lithium based electrolytes were used to avoid this complication. The first extensive study on the electrochemical reduction of thionyl chloride in various nonaqueous solutions was reported by Bowden and Dey[1]. They used various solvents including acetonitrile(ACN), N,N-dimethylformamide(DMF), methylene chloride(MC) and dimethylsulfoxide(DMSO). Using cyclic voltammetry(CV), coulometry and *ex-situ* UV-Vis spectroscopy, they concluded that a fairly long lived intermediate species, SO, is formed during the reduction of thionyl chloride. However, Dampier and Cole[2] ran similar experiments and concluded that there was no evidence of such an intermediate species. Later Go *et al.*[3] reported the evidence that, in dilute solutions, thionyl chloride forms an adduct with DMF molecules, *i.e.*, $SO^{2+} \cdot 2DMF$, liberating two chloride ions. Because of this species, they concluded that the first step of the electrochemical reduction of thionyl chloride in DMF can be described as

$$SO^{2+} \cdot 2DMF + 2e^- \longrightarrow SO + 2DMF$$

Propylene carbonate is an aprotic solvent with a moderately high dielectric constant and a wide liquid range. Many lithium salts are highly soluble in propylene carbonate.[10] It is stable toward lithum and has been one of the most widely used solvents in lithum battery research and technology.

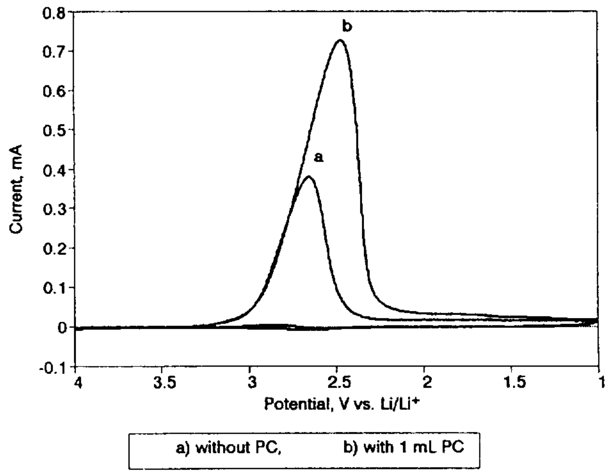

Figure 1. Cyclic voltammograms recorded from $SOCl_2$ (a) and 10% propylene carbonate-90% $SOCl_2$ (b) solution contaning 1.5 M $LiAlCl_4$ as a supporting electrolyte at a scan rate of 50 mV/s.

We ran the electrochemical reduction of thionyl chloride in propylene carbonate(PC)-thionyl chloride cosolvent systems with 1.5 M $LiAlCl_4$ as a supporting electrolyte. In this experiment, a small amount of propylene carbonate was used as a cosolvent in order to evaluate its role as a cosolvent in determining the electrochemistry of the thionyl chloride reduction as well as projected current density. Here, we report the preliminary result showing how current densities are affected by $LiAlCl_4$ in the presence of a cosolvent.

An OmniSolve, glass distilled, propylene carbonate(PC) was obtained from EM Science and was used after fractional distillation under helium atmosphere at a reflux ratio of 5 : 1. Electrochemical reduction of thionyl chloride was carried out by cyclic voltammetry techniques. A single compartment cell, which housed a glassy carbon working electrode (geometric area : 0.071 cm^2), a platinum wire counter electrode, and a Li wire reference electrode, was used for the electrochemical measurements in cosolvent systems containing 1.5 M $LiAlCl_4$ as a supporting electrolyte. Thionyl chloride (Aldrich, 99.9 %), aluminum chloride (Aldrich, ultradry, 99.99%), and lithium chloride (Johnson-Matthey, ultradry, 99.995%) were used to make up a 1.5 M $LiAlCl_4$ solution. All solutions were prepared in a glove box under an argon atmosphere. A Princeton Applied Research (PAR) model 273 potentiostat/galvanostat was used for recording cyclic voltammograms.

Figure 1 shows cyclic voltammograms of thionyl chloride reduction on glassy carbon electrode. The reduction of $SOCl_2$ in the absence of PC is shown by a curve with a clearly defined current maximum i_p at the potential E_p of about 2.69 V *vs.* Li. Introduction of 1 mL PC into the 9 mL $SOCl_2$ leads to an increase of the maximum peak current, but the peak potential shifts toward more negative potential.

The first voltammogram recorded in a freshly prepared $SOCl_2$ shows a large current peak as shown in Figure 2. The electrochemical process is irreversible as evidenced by the lack of the reversal current. Currents observed during subsequent scans are extremely low, at about one-tenth of the original current. If, after the first scan, the electrochemical cell is left undisturbed for more than 70 minutes with the circuit open, the large CV current observed in the first