

Fluorescence Study of Nano-scale Cyanine Dye Association Generated in Polymer Matrices. Size and Temperature Dependent Effects

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Nano-scale association of 3,3'-diethyloxadicyanin iodide (DODCI) is experimentally realized by several preparation procedures such as thin film formation with a hot-press process after coprecipitation of DODCI and a polymer. The size-dependent phenomena of the associated molecular aggregate having dimensions less than 100 nm have been found by performing optical measurements under controlled conditions over a wide range of the dye concentration and the temperature down to 8 K. We have proposed a model for the excited-state energy transfer kinetics between the monomolecule and the aggregate of DODCI, which can consistently explain the concentration and temperature dependence of fluorescence spectra and lifetimes we have investigated. The appearance of the nano-scale aggregate is predictable by using the model based on the analysis of the fluorescence intensity decay profile after a pulsed light excitation; the activation energy of 6.0—8.2 kJ mol⁻¹ for the excited-state deactivation processes of DODCI in poly(2-hydroxypropyl methacrylate) matrix have been obtained from the temperature dependence of the long and short fluorescence lifetime components and quantum yield. As the size of the aggregate or crystalline decreases, the fluorescence peak position has shifted toward shorter wavelengths, reflecting the confinement of the electronic state into an extremely small volume; the fluorescence peak wavelength varied from ~730 nm for the crystalline powder to ~640 nm for the small DODCI aggregate.

§1 Introduction

Nanometer-scale molecular aggregates composed of organic dyes which are either dispersed in solid matrices such as polymer or suspended in solution are of current interest because of their novel characteristics fairly different from those of single molecules.^{1,2)} Such a microscopic substance constituted from molecular building blocks by cohesive forces among them might be called 'supramolecule,' because the physical and chemical properties are beyond simple summation or extrapolation expected from the common knowledge about monomolecule or bulk crystal.³⁾ The actual molecular aggregate formed through a specific

association mechanism in matrices has a definite internal molecular order depending on the shape of molecules, interactions between them, and formation processes. Photoresponses, such as absorption and fluorescence, contributed by each molecule in the aggregate are greatly affected by the self-organized local environment and altered from those for an isolated molecular state. If it is experimentally possible to vary the size of the aggregate, say, between ~ 1 nm and ~ 100 nm, the number of molecules in it is varied widely from several to that for crystalline anywhere less than hundred thousands. We have already developed the versatile technique that uses coprecipitation and hot-press methods to treat organic dye-polymer mixtures.^{4,5)} By applying this to the case

of 3,3'-diethyloxadicarbocyanine iodide (DODCI) dispersed in a variety of polymers, it has actually become possible to control the size of aggregates in the polymer matrix and to change substantially the steric interactions between the polymer and the dispersed molecule or aggregate, which are a function of the concentration of the dye molecule and the type of matrix polymer. Photoresponses are sensitive to the association state of the dye molecule and, in order to analyze the related phenomena, we have to know physical parameters that can properly describe the characteristics of the condensed molecular system; we have utilized a few of these such as fluorescence peak wavelength, fluorescence decay profile, average association size, degree of molecular order, etc.

In the previous paper,^{6,7)} the basic aspects of DODCI nano-aggregate in various solid polymer matrices have been reported. Direct and intact observation of the condensed molecular aggregate of several to hundred thousands associated molecules by means of conventional measurements such as small angle X-ray scattering (SAXS) and electron microscope has long been hard to carry out. We could firstly estimate the particle size distribution of the DODCI aggregate by means of SAXS in the densely DODCI doped polymer films and also in the saturated solutions of DODCI, because the counter ion I^- of the dye moiety has fortunately a high X-ray scattering ability. However, the existence of a statistical distribution of the size seen in the SAXS data and inhomogeneous broadening of optical spectra even at low temperatures should be carefully examined to know the actual state of the molecular aggregate in the system prepared.

In order to know the supramolecular system composed of functional organic molecules under various microenvironments, the phenomenological analysis that can clearly categorize observable phenomena is important at the start of the investigation in advance of detailed microscopic or quantitative analysis. As for DODCI in a solid polymer matrix at a very low DODCI concentration ($<10^{-3}$ M), the optical properties such as absorption, excitation and fluorescence spectra, and fluorescence lifetimes are almost identical to those in dilute solutions and contrarily in the matrix with appreciably high DODCI concentration ($\sim 10^{-1}$ M), they become similar to those

inherent in a crystal. We can imagine that usual states are realized between the two extreme cases and the deviation can be experimentally traced by various photophysical measurements. We have carried out the experiment on temperature dependence of fluorescence spectra and lifetimes as well as the basic concentration dependence, and have related optical response changes of the system to the molecular association in polymer matrices occurring over a wide range of conditions.

§2 Experimental

Commercially available 3-ethyl-2(5-(3-ethyl-2(3H)-benzoxazolylidene)-1,3-pentadienyl) benzoxazolium iodide (3,3'-diethyloxadicarbocyanine iodide, DODCI; Exciton) was used without further purification. Three polymers were employed for the present work: poly(methyl methacrylate) (PMMA, MW=12,000; Aldrich), poly(benzyl methacrylate) (PBzMA, MW=54,000; Aldrich), poly(2-hydroxypropyl methacrylate) (PHPMA, MW=93,000; Aldrich).

Coprecipitation of DODCI and a polymer from several solutions was performed so as to make the dye molecule disperse in an appropriate polymer matrix in advance of further treatments: in a typical case, acetone was used as a good solvent common to the dye and polymer to make a mixed solution, and a large excess of hexane was used as a poor solvent to carry out precipitation.^{6,7)} The DODCI-polymer powder obtained by filtering was dried under vacuum keeping it just below the glass transition temperature (T_g) of the polymer.⁸⁾ A DODCI-polymer film of good optical quality with a thickness of several ten micrometers was formed from the DODCI powder sandwiched between thin glass plates by means of the hot-press (HP) method under vacuum.⁴⁾ The concentration of DODCI in the polymer film is calculated with the molar ratio of the starting materials when they are dissolved in the good solvent. High quality crystalline powders of pure DODCI were also produced by reprecipitation of the single component solution similar to the above-mentioned coprecipitation.

Small angle X-ray scattering (SAXS) of DODCI aggregates was used to evaluate their association size distribution (RINT-1500; Rigaku). X-ray diffraction from crystalline DODCI was measured on a

conventional diffractometer (RINT-2500; Rigaku). In respect of the DODCI aggregate embedded in a matrix, the measurable SAXS signal was mainly generated by iodide ions bound to the positively charged dye moieties due to the restriction for charge neutrality; the latter determined the basic structure of the aggregate through the molecular stacking like brickwork. The size distribution of a cloud of iodide ions was actually estimated by the slope analysis of an SAXS-intensity vs. scattering-angle curve using Guinier's law with the assumption of quasi-spherical association,⁹⁾ and the data have been cited in Table III of Ref.7

Absorption spectroscopy over visible and ultraviolet wavelengths and fluorescence spectroscopy over visible wavelengths were carried out on a commercial spectrophotometer (U-3400; HITACHI) and fluorescence spectrophotometer (MPF-4; HITACHI), respectively.⁷⁾ Time resolved fluorescence analysis was performed by a combination of a pulsed diode laser (PLP-02; Hamamatsu Photonics: oscillation wavelength ~ 632 nm fixed, pulse width ~ 67 ps) with a time-correlated single-photon counting system (TC-SPC; ORTEC).¹⁰⁾ We have adopted Eq 1 shown in the next section for the time response of fluorescent centers to a extremely short excitation light-pulse and the data have been deconvoluted taking account of the real shape of the excitation light-pulse with a software which could minimize residual errors. Fluorescence decay data at each dye concentration was, at first, fitted with a single exponential decay curve and, if an observable deviation was found, fitted with a double exponential decay curve by adding a shorter lifetime component with a proper weight. Relative fluorescence quantum yield compared with the one at room temperature was estimated by the ratio of the collection time for accumulating a preset total photon count at an appropriate wavelength in TC-SPC measurement. Fluorescence spectroscopy and time resolved fluorescence analysis at low temperature (LT; 8 K) were achieved with a closed cycle refrigerator system (CCS-350; JANIS) which was combined with either MPF-4 or TC-SPC/PLP-02. Several data discussed in the following section occasionally show a little incompleteness among them which may be due to inevitable difficulty in restoring exactly the same

sample conditions for different series of experiments, although the results are qualitatively consistent and enough for discussions: e.g., the dispersed DODCI concentration in the film could not be rigorously made the same as that inferred with the weighed amount ratio before various film formation procedures, and fairly different setups of the detection systems such as under ambient conditions and in cryostat changed spectroscopic sensitivity.

§3 Results and Discussion

3.1 Generation of DODCI association depending on the DODCI concentration and the surrounding materials

The size distribution of DODCI nano-scale aggregates has been investigated by means of small angle X-ray scattering (SAXS) measurement, and the molecular level interaction in the aggregate has been analyzed by ¹H NMR and solid-state ¹³C NMR spectroscopy in the previous reports.^{6,7,11)} Diameters of X-ray scatterers produced from DODCI molecules in a reprecipitate (crystalline powder), solutions, and polymer matrices have been cited in Table III in Ref.7. The different values in the first three columns in the table are to describe the distribution of association size and the last column shows a weighted average.

Photophysical properties of ideally dispersed monomolecular dyes in polymer matrices can be studied with advanced spectroscopy such as photochemical hole burning experiment,¹⁶⁾ but, in respect to the system containing various dye aggregates, relations between optical properties and the molecular state in the aggregate, such as the correlation between the maximum wavelength of the fluorescence spectrum and the size of each aggregate, and dependence of the fluorescence lifetime on the distribution of aggregates and monomolecules in the matrix, must be known at first on a clear experimental basis. The structure of the DODCI aggregate and the molecular interaction of DODCI with the polymer matrix are determined by a subtle balance between the self-organizing ability of DODCI and the affinity between the polymer matrix and DODCI, and also depend on the history of thermal treatment applied to produce the sample films. In the case of organic

compounds which form van der Waals-type crystals with a low melting or sublimation temperatures, sublimation due to the high vapor pressure and the spatial diffusion of constituent molecules in space are commonly observed for most phases such as crystalline and dispersion in solid matrices, so that the system is unstable under ambient conditions.⁵⁾ On the contrary, ionic compounds like DODCI have far more rigid crystalline state and the association structure is firmer than the van der Waals-type molecular crystals because of the existence of an electrostatic force for the association of molecular units. Based on such fundamental characteristics of organic compounds together with good characteristics of polymers as a very stable host material, we have developed the new film formation process to constitute the nano-scale supramolecular system without using conventional processes such as spin-coating, dipping, and spreading.⁷⁾

The wavelengths at absorption and fluorescence intensity maximums (λ_{\max}) are a measure of the average energy position of electronic transitions of the DODCI monomolecule and the DODCI aggregate which has a variety of association states and is surrounded by various microenvironments of matrix polymers produced through preparation processes; the fluorescence lifetime (τ_{em}) supplies valuable information on radiative and nonradiative deactivation processes and energy transfer processes from the photoexcited electronic states to a ground state or

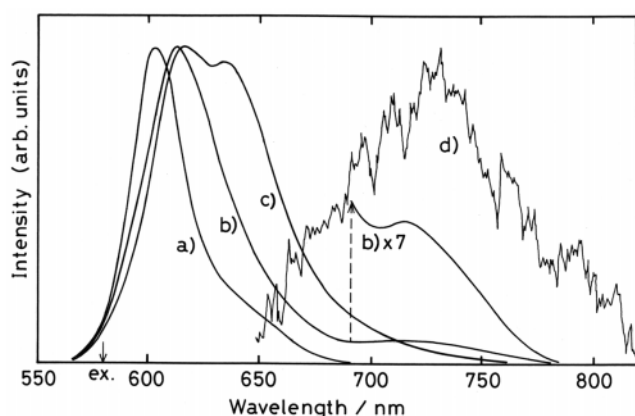


Fig.1 Comparison of various fluorescence spectra observed at room temperature in the monomolecular DODCI (a), 1×10^{-1} M DODCI-PMMA film (b), 2.5×10^{-2} M DODCI-PHPMA film (c), and crystalline powder (d), where the noise level of (d) shows an extremely low fluorescent intensity compared with the others.

energy acceptors. Typical fluorescence spectra at room temperature in several samples which will be discussed hereafter are shown in **Fig.1**.

By using the hot-press method, it has become possible to produce DODCI aggregates of various sizes in the polymer matrix at a fairly high DODCI concentration which cannot be attained by the other conventional methods. We found comparatively 'large' aggregates which were weakly fluorescent contributing to a fluorescence shoulder around 710 nm with average diameters of ~ 14 nm for the DODCI-PMMA films and ~ 12 nm for the DODCI-PBzMA films at the DODCI concentration as high as 0.1 M, while we predicted a smaller aggregate which was efficiently fluorescent contributing to a fluorescence peak around 640 nm, probably having an average diameter less than 2 nm, for the DODCI-PHPMA film at the same level of DODCI concentration.⁷⁾ The overall DODCI concentration dependence of the fluorescence λ_{\max} and lifetime τ_{em} in PMMA, PBzMA, and PHPMA films has been shown in Fig. 7 of Ref. 7. Similar dependence was also observed for the other polymers (PS, PPhMA, and VYHH).⁶⁾ **Table 1** summarizes the variation in optical responses of these films at various DODCI concentrations at room temperature and 8 K. In a very low DODCI concentration region less than 1×10^{-3} M, DODCI molecules are thought to be dissolved monomolecularly in the PMMA and PHPMA matrices, since the fluorescence λ_{\max} was almost the same as that in dilute solutions and the lifetime τ_{em} could be estimated by single exponential fitting. The monomolecular fluorescence band always persisted even in the very high DODCI concentration range where the additional fluorescence band due to the DODCI association appeared.

As clearly seen from the case of the PMMA film in Table 1, the monomolecular fluorescence band peak at $\lambda_{\max} \sim 600$ – 610 nm gradually shifted to longer wavelengths with increasing the DODCI concentration before the fluorescence from the coexisting aggregates appeared. This means that weak molecular interactions such as an induced dipole-dipole interaction between nearby monomolecules in the matrix may perturb the energy level of the electronically excited state and the ground state, thus showing larger Stokes shifts of the fluorescence band, and this may be a precursor of the

Table 1 The excitation and fluorescence peaks λ_{\max} , the lifetime τ_{em} , and the quantum yield ϕ_{em} at room temperature (RT) and 8K for the DODCI reprecipitate and the polymer films with various dispersed DODCI concentrations.

DODCI-Matrix	λ_{\max} /nm				τ_{em} /ns ^{b)}			ϕ_{em}
	Excitation		Fluorescence ^{a)}		RT	8K	Ratio	Ratio
	RT	8K	RT	8K	$\tau_{\text{em}}^{(s;l)}$	$\tau_{\text{em}}^{(s;l)}$	8K/RT	8K/RT
Reprecipitate	/ ^{d)}	/ ^{d)}	730	708+734	@740nm ^{c)}	@740nm	1.9;---	0.60
PMMA film								
[DODCI]					@640nm	@640nm		
1.0x10 ⁻¹ M	665	654	625;645;(705)	(625);648;(705)	0.17;1.0	0.21;1.12	1.2;1.1	3.3
1.0x10 ⁻² M	624	615	622; <u>643</u>	621; <u>641</u>	2.7	2.9	1.1	0.91
5.0x10 ⁻³ M	617	612	621	620;(640)	2.7	2.9	1.1	0.70
1.0x10 ⁻³ M	593	589	599	598	---	---		
PBzMA film								
[DODCI]					@640nm	@640nm		
5.0x10 ⁻² M	605	605	623;(715)	624;(705)	0.40;1.1	0.6;2.2	1.5;2.0	1.0
1.0x10 ⁻² M	606	604	622;(700)	622;(695)	0.45;1.45	0.7;2.5	1.6;1.7	1.1
1.0x10 ⁻³ M	607	607	613	612	0.50;2.3	0.5;2.8	1.0;1.2	1.7
PHPMA film								
[DODCI]					@640nm	@640nm		
1.0x10 ⁻¹ M	650	645	640	644	0.17;1.0	0.24;1.35	1.4;1.4	3.8
2.5x10 ⁻² M	631	624	615; <u>640</u>	618; <u>638</u>	0.80;2.2	2.3;3.5	2.9;1.6	3.5
1.0x10 ⁻³ M	599	590	611	608	2.5	2.5	1.0	3.5

a) + indicates the splitting of the fluorescence band, semicolon shows λ_{\max} (monomolecule); λ_{\max} (aggregate), and the value in the parentheses indicates a shoulder in the spectrum. The underlined peak became dominant with changing the excitation wavelength from 550 nm to 500 nm. b) Excitation was performed with a pulsed laser diode at 632 nm. Semicolon shows the short and long lifetime components $\tau_{\text{em}}^{(s;l)}$ for the main fluorescence band. --- shows insufficient fluorescence intensity to estimate the lifetime. c) Wavelength for the fluorescence lifetime monitoring. d) The excitation yield increased toward the fluorescence band wavelength without a distinct peak.

tight-bound aggregate formation. Since the absorption spectrum is hard to obtain in the high DODCI concentration film, the excitation peak wavelength is added in Table 1 for reference though the peak does not coincide with the absorption peak except for the case of a very low dye concentration.

The occurrence of DODCI association with the increase in the DODCI concentration is clearly predicted by looking at the lifetime change in the

fluorescence of the monomolecule and aggregate at a fixed wavelength, e.g., 640 nm, where its decay starts to deviate from a single exponential function to a double exponential decay characteristic, as well as the change in the spectral profile of the fluorescence: the lifetime in the PMMA film became double exponential when the large aggregate (λ_{\max} ~705 nm) appeared, and in the PHPMA film, when the small aggregate (λ_{\max} ~ 640 nm) appeared. The overlap of the two kinds of

fluorescence bands does not affect this qualitative conclusion as will be mentioned later. The PBzMA film occupied a special position, since the lifetime was always of two components over the examined DODCI concentration range. Considering that the fluorescence band at around 700 nm was seen even at 10^{-2} M DODCI, the aggregate is effectively generated in this matrix from very low doping density of DODCI and it was difficult to prepare the film in which DODCI was in complete monomolecular dispersion.

The change in the fluorescence spectrum in the PMMA film is fairly drastic, beginning at the DODCI concentration of about 10^{-2} M DODCI with the appearance of the 640 nm-band and finally the additional 705 nm-shoulder. The lifetime τ_{em} in the PMMA film becomes double exponential at 0.1 M DODCI, clearly indicating the formation of the large DODCI aggregate, the existence of which has been proven by SAXS measurement at the same DODCI concentration. The new fluorescence band at $\lambda_{max} \sim 700$ —715 nm observed in the densely DODCI-doped PBzMA and PMMA films with the DODCI concentration higher than 10^{-2} M is assigned to the fluorescence from an appreciably large nano-scale aggregate or an ultrafine crystallite formed in the polymer matrix in a self-organized manner, because the DODCI crystalline of the reprecipitated powder contributed to the similar fluorescence band at about 730 nm.

Although no aggregate with diameters larger than 2 nm was detectable by SAXS measurement in DODCI-PHPMA films as shown in Ref.7, another change in the fluorescence spectrum different from the above-mentioned large aggregate was found above 2.5×10^{-2} M DODCI: this new type of fluorescence band which appeared at $\lambda_{max} \sim 640$ nm and became dominant at 0.1 M DODCI seems to correspond to an extremely 'small' size aggregate or possibly fluorescent DODCI oligomer, although the DODCI dimer¹²⁾ is non-fluorescent. We have also found a similar fluorescent band in the saturated solutions of DODCI whose solvents are dimethyl sulfoxide, acetonitrile, dichloromethane, and trichloromethane, which means the microenvironment provided by the PHPMA matrix is similar to the one produced by these solvents. The fluorescence band at 643 nm appeared in the 10^{-2} M

DODCI-PMMA film at room temperature may have the same origin as these, though the lifetime remains almost single exponential at the DODCI concentration. Fluorescent isomer of the DODCI monomolecule considered by several authors^{13,14)} does not explain the concentration dependent new fluorescence we have observed and further the isomerization that rapidly changes the molecular conformation is improbable in the rigid matrix like the polymers examined here.

As has been discussed hitherto, the preparation method of films and the choice of matrix substances were so important for our study that we summarize some characteristics of the matrices we have used to produce the molecular association of DODCI, i.e., PMMA, PBzMA, and PHPMA. PMMA, $-\text{[CH}_2\text{C(CH}_3\text{)(COOCH}_2\text{)]}_n-$, which has a methyl substituent in a polymethacrylate chain, becomes frequently a standard matrix to make a comparison between various solid-state properties, since the physical and chemical data of PMMA have been well known.¹⁷⁾ The solubility of DODCI in PMMA was appropriate for our purpose and we could produce the DODCI-dispersed PMMA film over a very wide range of the DODCI concentration. In order to stabilize the molecular state of an ionic compound like DODCI, polarity, hydrophobicity, and hydrogen-bonding ability of the matrix may be essential factors. PMMA provides a rather nonpolar environment for DODCI due to the methyl substituent, so that the self-organizing force of DODCI in the PMMA matrix naturally leads to the occurrence of ordered aggregates with about 10-nm dimensions, which can be caused by the stabilization of charged ionic pairs, DODC^+I^- , in the nonpolar matrix to the molecular association.

PBzMA, $-\text{[CH}_2\text{(CH}_2\text{)(COOCH}_2\text{)}\phi\text{]}_n-$, which has a bulky benzyl substituent, forms a very hydrophobic environment, and the steric hindrance of the bulky benzyl may make the formation of the DODCI aggregate easier. This is reflected in the persistent existence of the DODCI aggregate in the PBzMA matrix down to a low DODCI concentration, where the fluorescence decay of the monomolecule still has two lifetime components showing the existence of DODCI aggregate, so that PBzMA is thought to be a proper matrix polymer to produce a large amount of aggregates between the high DODCI concentration and

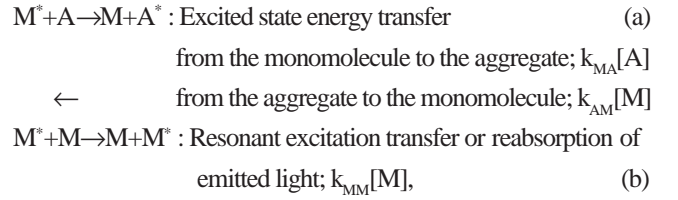
the DODCI concentration as low as 10^{-3} M. PHPMA, $-\text{[CH}_2(\text{CH}_3)(\text{COOCH}_2\text{CH}(\text{OH})\text{CH}_3)]_n-$, on the other hand, forms a little hydrophilic environment due to the hydrogen-bonding ability of hydroxypropyl and the PHPMA matrix was revealed to dissolve DODCI most efficiently among the polymers examined. This situation for the PHPMA matrix is well elucidated by the absence of a large crystalline aggregate detectable by SAXS measurement, though we believe that a type of ultrafine aggregate smaller than 2 nm contributing to the fluorescence band around 640 nm (Fig.1(c)) is stabilized.

3.2 Excited state energy transfer model

Except for the PBzMA film which did not contain the small aggregate represented by the 640 nm-fluorescence, there occurred at the high DODCI concentration the overlap of the monomolecular and small-aggregate fluorescence bands having the peaks at ~ 615 nm and ~ 640 nm respectively, the latter being the wavelength where the fluorescence decay was frequently monitored. Nevertheless, we determined the lifetime constants independently of whether the fluorescence band overlaps or not, and we thought the generation of the molecular aggregate predictable in all the DODCI-polymer films by monitoring the change in fluorescence decay profile at an appropriate wavelength with taking no account of the complexity of the fluorescence spectrum.

In order to reasonably understand such fluorescence lifetime characteristics and the excited state energy relaxation in the complex DODCI-matrix systems under various conditions, we have adopted a sufficiently generalized model which may cover most phenomena observed in our optical measurements. For this purpose, it is necessary to include the DODCI monomolecule, M, with the absorption $\lambda_{\text{max}} \sim 590\text{--}610$ nm and the DODCI aggregate, A, with the absorption $\lambda_{\text{max}} \sim 600\text{--}670$ nm; their photoexcited states, M^* , with the fluorescence $\lambda_{\text{max}} \sim 600\text{--}625$ nm and the lifetime $\tau_{\text{em}}^M = 1/(k_r + k_n)$, and A^* , with the fluorescence $\lambda_{\text{max}} \sim 640\text{--}715$ nm and the lifetime $\tau_{\text{em}}^A = 1/(k_r' + k_n')$, behave as the fluorescent centers, where k_r 's and k_n 's are the radiative and nonradiative transition rates, respectively. In addition to these, essential processes which determine the fluorescence

intensity change are:



where k 's are the transfer rate of the excited state and $[A]$ and $[M]$ are the concentration of A and M. If only the monomolecule, M, is excited by δ -function-like light pulse in the absence of the aggregate, A, the fluorescent time-response of the excited monomolecule, $I_M(t)$, is described simply by

$$I_M(t) \propto \exp(-t/\tau_{\text{em}}^M).$$

It is naturally presumed from the absorption and excitation band wavelength of M and A, and also the fluorescence band wavelength of M^* and A^* , that the excitation transfer by dipole-dipole interaction occurs very efficiently from M^* to A, i.e., k_{MA} in process a is expected to be large. For most realistic cases containing M and A, both of which can be photoexcited, we can very generally apply a double exponential decay function for the fluorescence decay of M^* :¹⁰⁾

$$I_M(t) \propto \exp(-t/\tau_{\text{em}}^1) + F_M \cdot \exp(-t/\tau_{\text{em}}^s), \quad (1)$$

τ_{em}^1 , long lifetime; τ_{em}^s , short lifetime; F, amplitude factor. τ_{em}^1 and τ_{em}^s are the functions of τ_{em}^M , τ_{em}^A , k_{MA} , and k_{AM} , and written: $1/\tau_{\text{em}}^{s,1} = 1/2 \cdot (\nu + \nu) \pm 1/2 \cdot \{(\nu - \mu)^2 + 4k_{MA}[A]k_{AM}[M]\}^{1/2}$, (2) and

$$\mu = 1/\tau_{\text{em}}^M + k_{MA}[A], \quad \nu = 1/\tau_{\text{em}}^A + k_{AM}[M].$$

If $1/\tau_{\text{em}}^M + k_{MA}[A] \gg 1/\tau_{\text{em}}^A + k_{AM}[M]$ and $1/\tau_{\text{em}}^A \gg k_{AM}[M]$ are satisfied and process b discussed later is negligible, then $\tau_{\text{em}}^{1,s}$ is simply written:

$$1/\tau_{\text{em}}^1 \sim 1/\tau_{\text{em}}^M + k_{MA}[A] \text{ and } 1/\tau_{\text{em}}^s \sim 1/\tau_{\text{em}}^A.$$

The form of Eq 1 is very versatile for the phenomenological analysis of the experimental data of complex systems as has been studied here. In respect of the fluorescence decay of A^* , we readily obtain $I_A(t)$ by substituting the suffix M for A, which gives the same τ_{em} 's and different F. Therefore, even when the fluorescence from M^* and A^* overlaps and the pulsed light is absorbed by both M and A simultaneously, the sum intensity, $I_M(t) + I_A(t)$, monitored at an appropriate wavelength is again described by the same form as Eq 1 where the F value becomes a formal fitting parameter. Because we discuss about changes in τ_{em} 's, not the F value, it is not necessary to consider much whether the

fluorescence from M^* and A^* at the monitoring wavelength is overlapped or not: F values are not cited in Table 1 for this reason.¹⁰⁾

Although the spatial diffusion of dye molecules is hard to occur in the rigid matrix, energy transfer due to process b between the monomolecules at the high DODCI concentration results in a time-dependent diffusion of the excited state population of M^* in space and causes a fluorescence decay which is not described by Eq 1. Based on the rigorous formulation of excited state deactivation taking account of this transient effect, it has been shown that such a component of fluorescence decay is always smeared out very rapidly and the decay component following the long lifetime constant, τ_{em}^1 , becomes soon dominant after a time elapse.¹⁸⁾ Equation 1 is widely applicable in good approximation when the long lifetime component has an order similar to the lifetime of M^* , i.e., $\tau_{em}^1 \sim \tau_{em}^M$, and $\tau_{em}^1 \gg \tau_{em}^s$, where the second exponent factor, τ_{em}^s , which is an additional short lifetime component, represents qualitatively the early-time transient effect. We can gain no further insight into the system by the successive addition of another exponent for higher approximations, though it is possible to carry out by a numerical procedure. Consequently, the problem is seen very perspectively by using the double exponential analysis for all the data over a very wide range of DODCI concentration and for a variety of polymer matrices at a variety of temperatures.

The radiative transition rate of M^* , k_r , which is estimated in Ref.19 and also evaluated by the integrated intensity of the absorption band spectrum of M, is of the same order as the $1/\tau_{em}^M$ obtained in this experiment, so that the nonradiative transition rate, k_n , is comparable to or much less than k_r , as $k_r+k_n=1/\tau_{em}^M$, that is, the monomolecule is an efficient fluorescer. As for the radiative transition rate of A^* , the quantitative estimation as the above was difficult to make. The overlap of the absorption bands of M and A and the persistent existence of the monomolecule over the whole DODCI concentration range prevented the examination of deactivation characteristics of the A^* fluorescence independently of the M^* fluorescence. Considering the data of the powdered crystalline, the very short lifetime is expected for the photoexcited aggregate if the molecular stacking similar to the

crystalline is realized. Possibly, excitonlike excitation energy transfer through molecular interactions in the aggregate becomes an important factor as well as the other energy deactivation. In spite of such ambiguity, $\tau_{em}^M \gg \tau_{em}^A$ is thought to be reasonably satisfied and the final results for the fluorescence decay characteristics are describable by Eq 1 and the approximation is good between room temperature and 8 K.

Based on both the assumed model and the measured data, it has been concluded that the concentration at which the one-component decay is switched to the two component one is where the DODCI aggregate starts to interact appreciably with the excited state of the monomolecule. This crossover concentration for the DODCI-polymer matrix system aligned as PBzMA<PMMA~PHPMA, while the size of the DODCI aggregate in the most densely DODCI-doped polymers estimated by SAXS measurement ranked as PMMA>PBzMA>>PHPMA. This shows the particle size and density of the generated aggregate in the matrix is not the monotonic function of the DODCI concentration initially introduced into the films.

3.3 Effects due to temperature reduction

To see the overall temperature effect upon the molecular systems, the excitation and fluorescence properties of the DODCI reprecipitate and the DODCI-polymer films at room temperature (RT) and 8 K are compared in Table 1. The low temperature effect on the reprecipitate was the τ_{em} lengthening by 1.9 times with 740-nm monitoring; there was no notable change in the excitation spectrum, but the spectral shape of the fluorescence band altered at 8 K. The reason why the lifetime of the reprecipitate becomes of two components is unclear though correlated with the split of the fluorescence band at 8 K. The increase in τ_{em} at low temperature with long-wavelength monitoring was experimentally common in crystalline states such as fairly large crystal, ground crystal and reprecipitated powder. To judge with the semiconductor band-edge fluorescence by analogy,¹⁵⁾ the fluorescence-band shift toward shorter wavelengths and the lifetime lengthening in the band-edge transition are expected with the reduction of the temperature if the crystalline ordering or molecular stacking of the dye molecule

induces a band-like energy level inferred by a structureless broad-band absorption. The τ_{em} value of the reprecipitate has shown weak dependence on the distribution of crystalline size. The ratio of the quantum yields, $\phi_{em}(8\text{ K})/\phi_{em}(\text{RT})$, for the reprecipitate was 0.6; curiously, it was less than unity and this might be due to the deactivation through imperfection of the crystalline though not definite.

In the dilute DODCI-polymer films containing less than 5×10^{-3} M DODCI, there was little low temperature effect on λ_{max} and τ_{em} , while the ratio of the fluorescence yield, $\phi_{em}(8\text{ K})/\phi_{em}(\text{RT})$, varied over 0.7—3.5. The matrix dependence of the ratio may become a qualitative measure to classify the molecular microenvironment around the monomolecule or the quality of matrix. For a normal monomolecular state of DODCI, the percentage of the excited state which nonradiatively decays by various thermally activated processes should decrease toward low temperatures and in effect ϕ_{em} will increase: this was realized in the DODCI-PHPMA and DODCI-PBzMA films, giving a ratio of 3.5 and 1.7 respectively, but was not applicable to the DODCI-PMMA film. Considering all the factors, DODCI is thought to be monomolecularly dispersed at least in PMMA and PHPMA in the dilute limit. If the homogeneous broadening of the optical spectrum of DODCI due to the matrix phonon (thermal vibration of the polymer chain) at an extremely low temperature becomes competitive with the inhomogeneous broadening due to statistical fluctuations in electrostatic potential of the matrix microenvironment around the dye molecule, the temperature decrease will induce narrowing of the monomolecular fluorescence band. Because such effect has not been observed for all the DODCI-polymer systems, the inhomogeneous broadening is much larger than the homogeneous broadening over the examined temperature range since most thermal motions are thought frozen at 8 K.

When the aggregate in the polymer films is generated with increasing the DODCI concentration, the lifetime τ_{em} became of the two components showing reasonably the existence of the DODCI aggregate and was elongated at 8 K: e.g., for the longer lifetime component, $\tau_{em}(8\text{ K})/\tau_{em}(\text{RT}) \sim 1.1, 2.0$ and 1.4 in 10^{-2} M DODCI-PMMA, 10^{-2} M DODCI-PBzMA, and

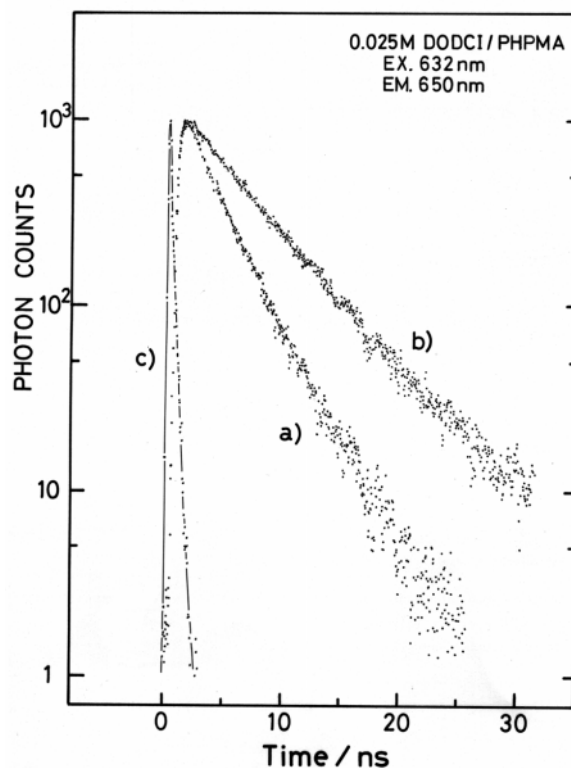


Fig.2 Typical fluorescence intensity decay profiles in the lifetime measurement for the overlapping monomolecular and aggregated DODCI fluorescence bands of DODCI-PHPMA films with 2.5×10^{-2} M DODCI at room temperature (a) and 8 K (b). The wavelength of the excitation light pulse (c) was 632 nm and the fluorescence intensity was monitored at 650 nm.

2.5×10^{-2} M DODCI-PHPMA, respectively. As the temperature of the DODCI-PBzMA film with 5×10^{-2} M DODCI was decreased from room temperature to 8 K, the fluorescence λ_{max} at 715 nm of the aggregate band shifted to 705 nm and both the long and short lifetime components at the 640-nm fluorescence were elongated, while the position of the monomolecular fluorescence band at 623 nm showed no noticeable change. In the DODCI-PHPMA film with 2.5×10^{-2} M DODCI, the coexistence of the monomolecule and the small aggregate at room temperature is very clearly shown by the contribution of the fluorescence bands at 615 nm and 640 nm, respectively (Fig.1c). The fluorescence spectrum at 8 K remained almost the same but the fluorescence lifetime was appreciably elongated as seen from **Fig.2**. Because the monomolecular fluorescence band observed singly at the low DODCI concentration showed little lifetime change with the temperature, the coexisting aggregate of the dye molecule is concluded to be the cause of the observed

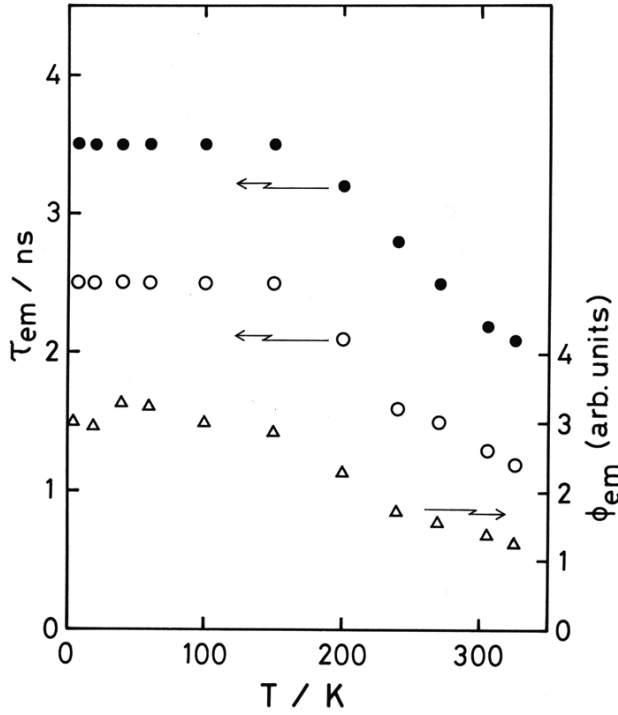


Fig.3 Temperature dependence of the fluorescence lifetimes τ_{em}^l (●) and τ_{em}^s (○), and the fluorescence yield ϕ_{em} (△) for the DODCI-PHPMA film with 2.5×10^{-2} M DODCI. The fluorescence was taken at 650 nm with 632-nm excitation.

temperature dependence of the lifetime.

The respective ϕ_{em} ratios seem to vary rather widely among the polymers: 1.0—1.7 in the PBzMA films, 3.5—3.8 in the PHPMA films, and 0.7—0.9 in the PMMA films except for the 0.1 M DODCI-PMMA film which has an abnormally large ratio of 3.3: the excess doping of DODCI into PMMA might induce an special effect on the matrix-dye interaction. Such situations are essentially attributable to the microscopic structure of the polymer matrices and their interactions with the dye aggregate which can be modified by pendent substituents of polymer chain as mentioned earlier. The reabsorption of emitted light in the very high optical density (OD) films may alter the apparent ϕ_{em} value but it does not explain the polymer dependence.

In the case of the 2.5×10^{-2} M DODCI-PHPMA film, the temperature dependence of the lifetime of the overlapped fluorescence emitted from the monomolecule and the small aggregate was fully measured at 650 nm between room temperature and 8 K as shown in **Fig.3** in spite of a very low detection efficiency from the small aperture inherent in the cryostat system, where the percentage of the two

fluorescence intensities changed with a monitoring wavelength but did not affect the result. The lifetime increased from the values at room temperature toward lower temperatures and the change was saturated below 165 K.

Based on the temperature dependence of τ_{em} and ϕ_{em} , we discuss further the excited-state deactivation processes to separate them into the one which can be thermally activated and the others. Although the actual lifetime constants are complex functions of many rate constants, k 's, these rates are phenomenologically separable into two parts which are temperature dependent and independent: e.g., the radiative transition rate of A^* , k_r , is temperature independent under normal conditions and most nonradiative transitions are thermally activated. We have described such essential behavior of $\tau_{em}^{l,s}(T)$ as a function of temperature, T , with

$$\tau_{em}^{l,s}(T) = 1 / \{k^{l,s} + k^{l,s}(T)\}, \quad (3)$$

where $k^{l,s}$ and $k^{l,s}(T)$ are the effective deactivation rates being independent of and dependent on temperature, respectively, and the superscripts, l and s , indicate the long and short lifetime components, respectively. Although this assumption oversimplifies the situation if the derivation of Eqs 1 and 2 is recalled, there comes out a good merit to extract a phenomenological parameter from the measured data which can characterize molecular interactions in the dye-polymer system. If the main process to determine the temperature dependence of $k(T)$ is the rate process having a representative activation energy, ΔE , we have

$$1/\tau_{em}^{l,s}(T) - k^{l,s} = k_0^{l,s} \cdot \exp(-\Delta E^{l,s}/RT), \quad (4)$$

where $k_0^{l,s}$ are the frequency factor for the deactivation. As for the fluorescence monitored at 650 nm in the 2.5×10^{-2} M DODCI-PHPMA film, the temperature variation in $\tau_{em}^{l,s}$ is saturated below 165 K as seen from **Fig.3**, and the temperature-independent $k^{l,s}$ value was readily known from these saturated values. **Figure 4** shows the logarithmic plots of $1/\tau_{em}(T) - k$ vs. $1/T$, from the slope of which we can obtain ΔE of Eq 4. The activation energies were $\Delta E^l \sim 8.2$ kJ mol⁻¹ for the long-lifetime component and $\Delta E^s \sim 7.9$ kJ mol⁻¹ for the short-lifetime component, which were very close to each other.

In order to correctly discuss the quantum yield, ϕ_{em} , we must take into account the situation that some

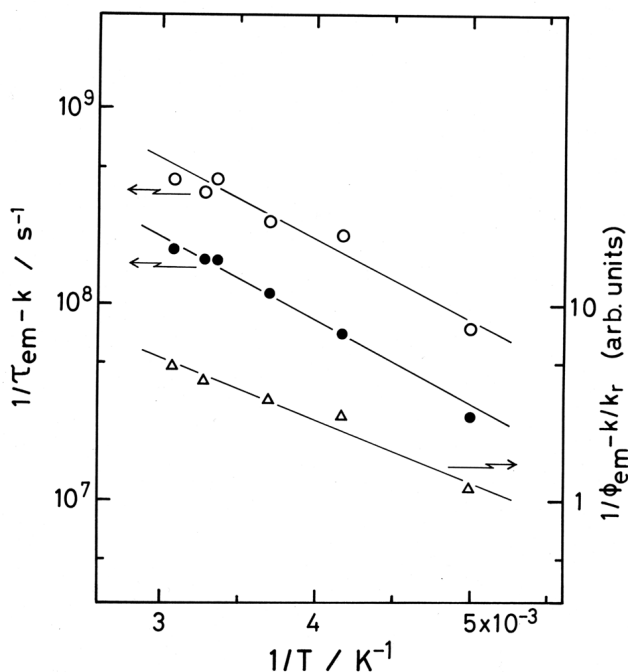


Fig.4 Logarithmic plots of $1/\tau_{em}^{ls} - k^{ls}$ and $1/\phi_{em} - k^*/k_r$ vs. $1/T$, where k^{ls} and k^*/k_r are estimated from the saturated values at the low temperature region in Fig.3. τ_{em}^{ls} (○), τ_{em}^s (●), and ϕ_{em} (△).

amount of M^* will suffer from the instantaneous quenching caused by a contact-type strong interaction between polymer chains and M^* at a confined small site which deactivates it directly to the ground state without fluorescence. This is the ‘static quenching’ factor described as process c:^{20,21)}



where $W = \exp(-V[\text{quenching site close to } M^*])$ is a factor dependent on the quenching site density close to M^* and the static quenching constant, V , indicating the strength of the quenching interaction between M^* and the quenching site. The fraction of W of M^* follows the normal deactivation processes discussed hitherto and the fraction of $1-W$ of M^* follows the instantaneous deactivation because it is inside the strong affection range of quenching sites. W is assumed to depend on the thermal fluctuation of polymer chains at the quenching site. Even if this factor is introduced, the conclusion obtained for the τ_{em}^s 's characteristics is not altered, but the resultant fluorescence intensity is reduced and the actual quantum yield is replaced by:

$$\phi_{em}(T) = Wk_r \tau_{em}^s, \quad W\tau_{em}^s = 1/\{k^* + k^*(T)\} \quad (5)$$

$$1/\phi_{em}(T) - k^*/k_r = k^*(T)/k_r = (k_0^*/k_r) \cdot \exp(-\Delta E^*/RT), \quad (6)$$

where k_r is the temperature-independent radiative

deactivation rate, and k^* and $k^*(T)$ are the corresponding effective deactivation rates being temperature independent and dependent. By introducing the static quenching process, it has become possible to explain the experimental result that the ϕ_{em} value is very sensitive to the type of matrix polymer and changes with T even if τ_{em} does not change with T as is the case for the very low DODCI concentration.

Experimentally, the temperature dependence of the relative ϕ_{em} value is measurable by monitoring the fluorescence intensity at an appropriate wavelength if the temperature change in fluorescence band spectrum is small. Concerning the quantum yield of the monomolecule, ϕ_{em}^M , at the low DODCI concentration, it behaved reasonably in the PHPMA film giving a larger value at low temperature but abnormally in the PMMA film giving a value less than unity at low temperature, considering the quenching effect will be suppressed at low temperature due to the decrease in the thermal fluctuation of the matrix media. This may be partly because the PMMA matrix is rigid compared to the PHPMA matrix and, without an appropriate amount of strain reducing additives, the static quenching centers such as microscopic cracks in the matrix increase in density or in quenching ability with the temperature reduction. If the high concentration of DODCI works as the strain reducer, the quantum efficiency recovered to the normal value as seen from Table 1 for the 0.1 M DODCI-PMMA film is rather reasonable.

The fluorescence from the DODCI-PHPMA film at 2.5×10^{-2} M DODCI which is monitored around 640–650 nm contains the components from the monomolecule and small aggregate, so that we have observed the sum of the ϕ_{em} values for these two species, i.e., $\phi_{em} = \phi_{em}^M + \phi_{em}^A$. Because of efficient fluorescence of the two components, the temperature change in ϕ_{em} can be experimentally traced, being saturated below 100 K similarly to τ_{em}^s : the k^*/k_r value was readily estimated from this saturated value. The logarithmic plot of $1/\phi_{em}(T) - k^*/k_r$ vs. $1/T$ is shown in Fig.4, from the slope of which we can obtain ΔE^* of Eq 6. The activation energy was $\Delta E^* \sim 6.0 \text{ kJ mol}^{-1}$.

The activation energies of $8.2 - 6.0 \text{ kJ mol}^{-1}$ of the same order were obtained for $\tau_{em}^{ls}(T)$, $\tau_{em}^s(T)$, and $\phi_{em}(T)$. It is noted that the values for τ_{em} and ϕ_{em} are

derived from the independent analyses and these values contain an important phenomenological meaning in relation to the microenvironment of the DODCI monomolecule and the DODCI aggregate in the PHPMA matrix. The activation energies are comparable to the hydrogen-bonding energies such as C-H \cdots N, C-H \cdots O, and O-H $\cdots\pi$ -electron which are all in the range of 5–20 kJ mol $^{-1}$, and it is conjectured that these intermolecular binding mechanisms or weak attractive forces which are effective between organic molecules possibly determine the temperature dependence of the lifetimes and quantum efficiency measured between room temperature and 8 K. It has already been shown from the NMR data in the previous report¹¹⁾ that the intermolecular binding through a hydrogen bond is important for the molecular association

In respect of the temperature change in τ_{em} , the dependence is mainly due to the lifetime change in τ_{em}^A of the aggregate, because τ_{em}^M of the monomolecule is temperature insensitive as seen from the results at $\sim 10^{-3}$ M DODCI in Table 1. The binding between the associated molecules would be loosen by the temperature elevation, which may induce the increase in deactivation rate by the fluctuation of the association structure. k_{MA} and k_{AM} which determine the excited state energy transfer between the monomolecule and aggregate are essentially temperature independent if the molecular conformation and relative position are fixed, but, as the structure of the aggregate thermally fluctuates, they contribute indirectly to temperature change in τ_{em} as well as the direct contribution from k'_n . We have known the large aggregate generated in these matrices has crystalline-like molecular ordering, since it has an fluorescence band around 700 nm similarly to the crystalline powder, and it might be natural that $\tau_{em}^1(T)$ and $\tau_{em}^s(T)$ which contain common terms expressed in Eq 2 have given the very similar values of $\Delta E^1 \sim 8.2$ kJ mol $^{-1}$ and $\Delta E^s \sim 7.9$ kJ mol $^{-1}$, respectively, but further experiments are needed to understand quantitatively which deactivation pathway is most effective and temperature-dependent in the dye-polymer system.

Generally, intersystem crossing between the electronic singlet and triplet states is thought to be an efficient mechanism for the monomolecular excited

state deactivation among the others. In the case of DODCI, the excitation transferred from singlet to triplet state decays nonradiatively because phosphorescence inherent in the triplet state has not been observed even at low temperatures. If contact or through-bond interactions such as the hydrogen bonding between the outer π -electron shell of DODCI and polymer chain pendants can thermally promote the intersystem crossing through the excited energy levels, they become a possible mechanism for the static quenching which has explained well the temperature change in ϕ_{em} and given $\Delta E^* \sim 6.0$ kJ mol $^{-1}$.

3.4 Excited state energy scheme of the DODCI-polymer system

In order to clearly understand the optical property of the DODCI aggregate-matrix system, we have proposed in Fig.5 an energy diagram which is consistent with the characteristics analyzed in this report including the excited-state energy transfer kinetics between the dispersed monomolecule and the randomly distributed aggregate. The energy levels for the ground and excited states are schematically shown as a function of the number of molecules, N, which spreads from monomolecule (N=1), dimer (N=2), oligomer or small aggregate (N= n_a^s), large aggregate (N= n_a^l), precipitate (N= $n_p \gg n_a$) to crystal (N= ∞): the ground states are drawn relatively shifted to lower energies with the increase in the molecular association

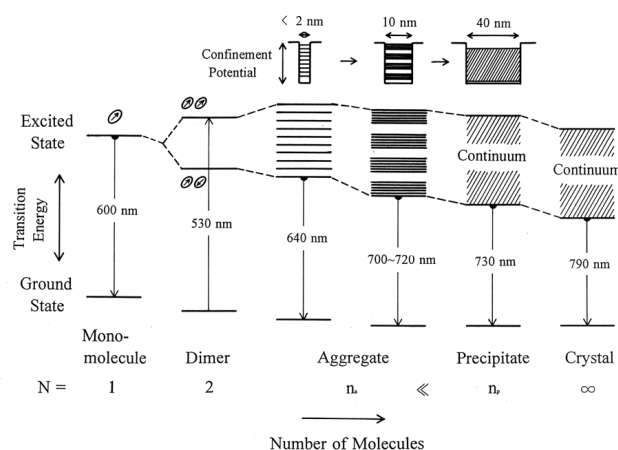


Fig.5 Schematic drawing of the change in electronic energy levels of DODCI molecules for various states according to the increase in the number of molecules in the aggregate. The typical transition energy from the excited state to the ground state in each case is indicated by the fluorescence peak wavelength.

number considering the stabilization with attractive forces in the association. The dimeric association of DODCI has been observed by absorption spectroscopy in several solutions of concentrated DODCI such as an aqueous solution¹²⁾ and also in polymers such as PHPMA. The excited state splits into two sublevels, an upper branch of which is dipole-allowed, but a lower branch of which is dipole-forbidden so that there is no fluorescence from the lower branch. The excited state of the aggregate having more than several molecules splits into much more sublevels depending on the molecular association number and becomes dipole allowed with appreciable fluorescence intensity.³⁾ The small aggregate found in the DODCI-PHPMA film has a fluorescence peak at a shorter wavelength compared to the large aggregate found in the DODCI-PMMA and PBzMA films because of the stronger confinement of electronic states in the smaller volume. The sublevels for a large size aggregate merge into a broad single band, or a continuum band, if the constituent molecule is closely packed as the DODCI crystal. The proposed energy scheme is sufficient for consistently explain the fluorescence spectrum change which is controlled by the DODCI concentration in the system and the energy deactivation kinetics of the photoexcited DODCI monomolecule and aggregate under various conditions.

§4 Conclusions

Excited-state energy deactivation mechanisms in various polymer films, where the DODCI aggregate coexisted with the DODCI monomolecule, were clarified by the optical data being dependent on the DODCI concentration in the film, pendant substituents of the polymer, and temperature reduction down to 8 K. The proposed reaction kinetics in the excited state could consistently explain all the phenomena experimentally examined. We could obtain the activation energy for the deactivation process of the excited DODCI monomolecule-aggregate system formed in the DODCI-PHPMA film with 2.5×10^{-2} M DODCI: $\Delta E^1 \sim 8.2 \text{ kJ mol}^{-1}$ for τ_{em}^1 , $\Delta E^s \sim 7.9 \text{ kJ mol}^{-1}$ for τ_{em}^s , and $\Delta E^* \sim 6.0 \text{ kJ mol}^{-1}$ for ϕ_{em}^* ; the value was comparable to the energy for hydrogen bonding which is thought to compose an important part of the interaction between DODCI molecules and polymer

chains. The DODCI concentration where the fluorescence decay after a light pulse excitation changes from single to double exponential time-decay profile has been a very clear measure of the generation of the DODCI aggregate or crystalline, as well as the change in the absorption and fluorescence spectra. We have proposed the energy diagram for various degree of the molecular association, which could explain very well the experimental results.

We believe that the ideally clean organic system made of the associated dye-molecule and the polymer matrix by means of the totally in-vacuum processes^{22,23)} will become more and more important in the work of engineering side as well as the basic investigation carried out here. We have clarified some aspects of the phenomena concerning nano-scale dye association, but further effort to analyze rigorously the internal structure and order of the involved molecules is required by using much advanced observation techniques such as optical near field scanning microscope with a nanometer resolution.

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