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Anomalous Association of 3,3'-Diethyloxadicarbocyanine Iodide in Saturated Solutions of Acetone and Water

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An association of 3,3'-Diethyloxadicarbocyanine Iodide (DODCI) in saturated solutions has been investigated by means of small angle X-ray scattering (SAXS), ^{1}H-NMR spectroscopy and photo-emission spectroscopy. In the investigation by SAXS, we have revealed that DODCI molecules in a saturated acetone solution exhibit an association with an average diameter of 4.5 nm, which is reasonably supported by ^{1}H-NMR spectroscopy and we could fairly well understand the structural hierarchy acting in the formation of the association.

In recent years, optical properties of associated molecules, e.g., J- and H-aggregates, have been widely investigated because localized electronic states in the associate, typically known as molecular exciton, excimer, etc., exhibit very interesting phenomena.1) A mesoscopic system composed of organic molecules less than about ten thousand molecules is a matter of current interest as well because of its novel optical properties quite different from those of a single molecule and a crystal.2) Being considered as the ultimate unit of tractable collection of atoms, a single organic dye dissolved in a solvent or a polymer matrix exhibits photoresponsive properties such as photo-absorption and photo-emission. These properties consequently yield exotic photochemistry and photophysics of solvatochromism,3,4) laser oscillation5) and so on. In some cases of molecular association of organic dyes, furthermore, photo-absorption and emission resulting from the association, ranging from a dimer molecule6) to crystalline aggregates of more than ten thousand molecules, have become readily observable. In these systems, molecular association must be considered to have structural hierarchy: at the molecular level, association number and orderliness of each molecule in the associate are important, and at the aggregate level "mesoscopic association mechanism" combining each associate is to be clarified. In the former, the most intriguing question is what mainly determines physical properties of the associate: whether the association number or the orderliness of each molecule. In the latter, electronic and electrostatic interactions both between the associates and between the matrix and the associate will be important. Anyway, it is essential to clearly elucidate structure and states of association in relation to observed physical properties of the associated molecules.

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. Emission and NMR spectra, and SAXS were measured for saturated DODCI solutions: solvents were spectral grade acetone, methanol (MeOH), dimethyl sulfoxide (DMSO), acetonitrile, tetrahydrofuran (THF), dimethylfolmamide (DMF), chloroform, and dichloromethane. Deuterated solvents were used for ^{1}H-NMR measurement with about 5 mg of DODCI in 0.5 ml solvents ($\sim$2x10^{-2} mol/l) for lower concentration solutions. Saturation of DODCI was checked by the deposited DODCI at the bottom. Absorption spectroscopy over visible and ultraviolet wavelength regions was carried out on a commercial spectrophotometer (U-3400; HITACHI); emission spectroscopy on a commercial fluorescence spectrophotometer (MPF-4; HITACHI). SAXS was measured for saturated DODCI solutions using a 3-slit goniometer with a rotating Cu anode (50 kv, 300 mA)(RINT-1500; Rigaku Co.).$^{7)}$ ^{1}H-NMR spectra were observed by a Bruker AC-200 at the resonance frequency of 200.13 MHz. The ^{1}H-NMR shifts were referred to the internal TMS in the organic solvents and D_2O.

An electronic transition of DODCI has been investigated by absorption spectroscopy in various solvents. An absorption spectrum in a dilute MeOH solution (OD$\sim$1) exhibited a maximum wavelength (λ_{max}) of 578 nm with full width at half maximum of about 35 nm, where the molar extinction coefficient in MeOH is 2.56x10^5 l/mol • cm at $\lambda \sim$578 nm. DODCI molecules in solvents showed only a small (23 nm) stokes shift. Solvatochromic shifts for both protonic and aprotic solvents were hypsochromic ones with the increase in the static dielectric constant (ε): for $CHCl_3$ ($\lambda_{max}\sim$592 nm, ε^{20}: 4.8), and for H_2O (576 nm, ε^{20}: 80.4), except for DMSO (589 nm, ε^{20}: 36.8). These hypsochromic shifts were also observed in the DODCI family: 3,3'-Diethyloxacarbocyanine Iodide, 3,3'-Dimethyloxacarbocyanine Iodide, 1,1'-Diethyl-2,2'-cyanine [Iodide, Bromide, and Chloride]. Though the hypsochromic shift was observed, the electronic transition of DODCI may be a π-π^* transition, judging from the very large extinction coefficient of the longer wavelength absorption. The association size of DODCI molecules in saturated solutions has been

Table 1. Solvent dependence of an average diameter of molecular association in solutions

Solvent	Diameter (nm)	Remarks
Acetone	4.5	Saturated
H_2O	4.1	Saturated
MeOH	< 2	Saturated
	< 2	near Satu.
CH_3CN	< 1	Saturated
DMF	< 1$^{a)}$	Saturated

a) A diffraction peak is never observed even in a saturated solution.

measured by means of SAXS as shown in Table 1. Sufficient amount of DODCI powder was put in a quartz capillary (inner diameter; 2 mm) with a solvent so as to leave deposits at the bottom and to attain equilibrium, where a measurable diameter by SAXS was between 2 nm and 100 nm in the present apparatus. Association of molecules was found out in saturated acetone (av. 4.5 nm) and H_2O (av. 4.1 nm) solutions, whereas no obvious small angle scattering was observed in saturated MeOH, acetonitrile, and DMF solutions. Since X-ray diffraction can be observed from particles larger than about 100 nm,$^{7)}$ the diffraction from the solution in the upper part of the sample capillary was measured for a DMF solution to check absence of molecular aggregates larger than 100 nm. While a diffraction with slightly shifted peak positions compared with powder crystal was observed from the deposited DODCI at the bottom, no diffraction was observed at the upper part of the solution. Microscopic environment of DODCI molecules has been clarified by ^{1}H-NMR spectroscopy in saturated and ~2x10^{-2} mol/l solutions. In the ~2x10^{-2} mol/l solution of acetone, the ^{1}H-NMR spectral pattern is similar to that of the other solutions such as $CDCl_3$ and MeOD solutions. When DODCI concentration in the acetone solution was increased, additional new peaks appeared as higher field shifted peaks for methyl (CH_3) (-0.37 ppm) and methylene (CH_2) (-0.8 ppm), whereas no additional peak was observed in $CDCl_3$, MeOD and deuterated DMSO even with the addition of 30 mg DODCI in 0.5 ml solvents(Fig. 1).$^{8)}$ On the other hand, additional peak positions of olefinic protons were shifted to lower fields: 1.0 ppm for α-CH= proton and 0.5 ppm for γ-CH= proton. The peak position corresponding to β-CH= is hardly changed. Little change was observed for aromatic protons. Because the ^{1}H-NMR shifts induced by the concentration change were very large, a type of association of DODCI molecules is assumed to emerge in the saturated acetone solution. There are two characteristic points for the induced shift: the directions of shifts are opposite for the ethyl protons and for the olefinic protons, and the magnitudes are alternative for CH_3 (-0.37 ppm), CH_2 (-0.8 ppm), α-CH= (1.0 ppm), β-CH= (~0 ppm) and γ-CH= (0.5 ppm). Due to the association of DODCI molecules, the electric charge on the olefinic part may be changed, which further

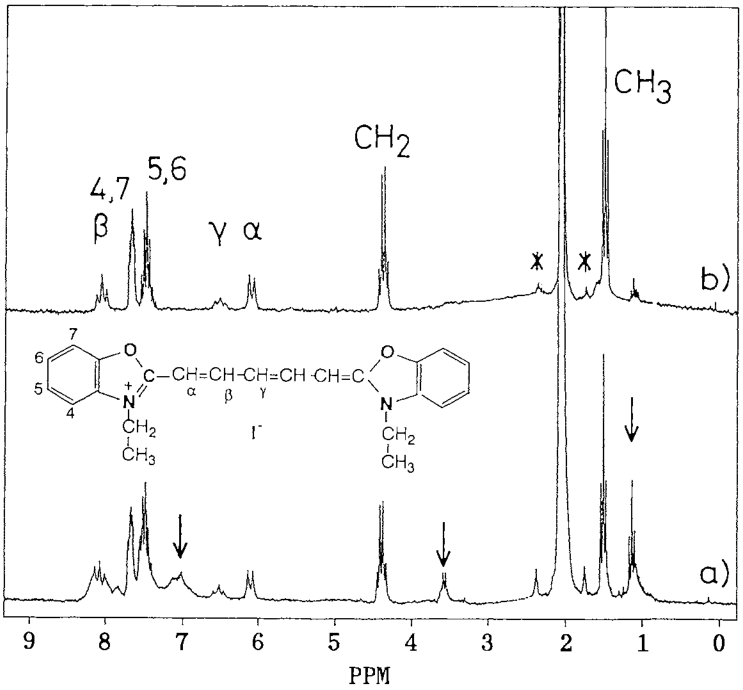

Fig. 1. ^{1}H-NMR spectra of DODCI/acetone-d_6 saturated solution (a) and ~ 2x10^{-2} mol/l solution (b). The additional peaks are shown by arrows, and (*) are spinning side bands of solvent.

affects the side-chain protons through nitrogen atom. Since the signals for the associated molecules are clearly observed with sharp line patterns, the states of associated molecules is considered to be a unique one, and we can estimate that about 30% of molecules are forming the associate in solution using integration of each shifted and unshifted peak intensity. Considering the large peak shifts, the preservation of sharp line pattern, and solubility in acetone, which is higher than in aqueous solution but lower than in $CDCl_3$, a basic unit for the association will be tight coupling of two or more DODCI molecules. Such brick units could further form a larger scale brickwork due to mesoscopic association mechanism through an electrostatic field, which may be observed as associates having a diameter of 4.5 nmϕ by SAXS measurement. The associates in a saturated acetone solution can be fixed in a solid state by using a reprecipitation method from the acetone solution (a good solvent) to n-hexane (a poor solvent). The associates and crystallines of DODCI molecules were observed in the precipitated powder of DODCI by means of SAXS and X-ray diffraction measurement, respectively.

An anomalous association of DODCI molecules with diameters of 4~5 nm in saturated acetone and aqueous solutions has been observed. The association state of DODCI molecules is concluded to be the association with structural hierarchy composed of strongly coupling two or more DODCI molecules. The reason why the DODCI associates exist only in acetone and water still remains an open question. Details of the association mechanism in those solutions will be revealed by precise measurements both on hysteresis in sample preparation and on temperature effect.

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