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Spectral properties and structure of the J-aggregates of pseudoisocyanine dye in layered silicate films

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ABSTRACT

Hybrid films composed of pseudoisocyanine (PIC) and layered silicates were prepared by direct adsorption from dye solution. Properties of the films were characterized by absorption and fluorescence spectroscopy, which indicated the formation of two types of J-molecular aggregates. Molecular arrangement and structure of the J-aggregates were investigated by means of linearly polarized absorption spectroscopy and X-ray diffraction (XRD). Structural models of the two main types of J-aggregates with oblique and those of parallel molecular alignments were designed. The spectral properties of these species were studied in detail. All the films contained a mixture of both types of the J-molecular assemblies. Predominance of either species likely depends on the layer charge of the silicate template.

1. Introduction

Pseudoisocyanine (PIC) dye (see supplementary information (SI) No. 1) attracts much attention due to its unique properties as well as industrial applications [1]. One of the most studied phenomena related to this dye is the formation of supramolecular assemblies called J-aggregates. The specific structures of the J-aggregates are typical of a head-to-tail intermolecular association between the molecular units [2]. Formation of the J-aggregates of PIC has been reported for various types of reaction systems, e.g., solutions [2,3] and interfaces [4]. Preference for the PIC cations to form J-aggregates rather than the generally more common H-aggregates is mainly due to the molecular structure of PIC (Fig. 1). The cations bear two hydrophobic ethyl groups, which are close to the center of the molecule, thus preventing formation of sandwich-type assemblies called H-aggregates [5]. The J-aggregates are true organic nanoassemblies [6]. Under specific conditions, they can be built from tens to thousands of assembled molecules and exhibit variable macrostructural features [7,8]. One of the main properties of the J-aggregates is the absorption spectrum: Light absorption by chromophores, which form J-aggregates, is characterized by a sharp spectral band of relatively high molar absorption coefficients and at significantly lower energies than the absorption associated with the transitions of individual (nonaggregated) dye cations [1,9]. Other properties include those having been observed for J-aggregates in general, such as fluorescence [10], spectral-hole burning phenomena [11], nonlinear optical properties [12,13] and energy transfer [14,15].

There have been numerous attempts to prepare various hybrid materials based on inorganic substrates with embedded organic dyes. Such materials could be applicable in modern industrial fields [16]. The inorganic substrate would provide an inert and optically inactive matrix. Hence, an advantageous property of such materials would be the isolation of dye molecules from the chemical environment. Inorganic carrier would neither directly contribute to optical properties of the material nor actively take part in photochemical processes. Potential stabilization of the chromophores against decomposition has already been observed for some cyanine dyes in layered silicate dispersions based on natural and synthetic clay minerals [5,17]. The preferential orientation of dye molecules on the inorganic substrate is another important property, which is expected for this kind of materials [18]. It could be very important for some applications in optics, where materials exhibiting optical anisotropy are required. Well-organized

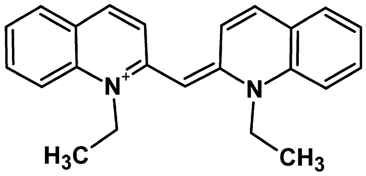

Fig. 1. Molecular structure of pseudoisocyanine cation.

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Table 1
Basic parameters of used layered silicates

Specimen	Symbol	CEC ($\text{mmol}\,\text{g}^{-1}$) with references	S_{ion} (nm^2)
Fluorohectorite	FH	1.50 [5]	0.44
Laponite RDS	L	0.87 [31]	0.75
Kunipia montmorillonite	K	1.15 [32]	0.54

Note. CEC, cation exchange capacity. S_{ion}, surface area occupied by one monovalent cation, i.e., to the average surface area per one electron charge.

J-type assemblies are formed on planar surfaces or can be stabilized as intercalated species on various substrates of layered, two-dimensional structures [19]. Layered inorganic compounds include phosphates [20], niobates [21], and silicates. The choice of an inorganic component is often a key factor in successfully preparing materials of optimal properties. One could note the swelling of the inorganic material, the property necessary for homogeneous and controlled dye intercalation [22,23], charge of the layered templates, controlling the distribution of the dye cations [16], and structural properties of the surface [24].

There have been several attempts to prepare various hybrid materials based on PIC or other cyanine dyes and inorganic layered compounds [25–28]. Detailed studies have been aimed at the interaction with layered silicates (mostly represented by clay minerals) in aqueous dispersions [5,29]. Partial decomposition of PIC was observed in diluted layered silicate dispersions. The decomposition was specifically related to the layer charge density of the inorganic component [5]. The effects of other properties and parameters on the formation of J-aggregates were claimed in another study [30]. Intercalation of the PIC was achieved also in a poorly swelling sodium titanate with preadsorbed propylammonium cations [18,22]. Inorganic silicate magadite grafted with hydrophobic alkyl chains exhibited significantly different properties for the intercalation of PIC cations [31]. More knowledge on the formation and structural aspects of the PIC J-aggregates has been published for the systems of mica [24,32] and glass [33] surfaces.

The objective of this work was to shed more light on the formation, structure, and properties of thin films of layered silicates with intercalated PIC J-aggregates. The preparation of the hybrid materials was achieved via a direct PIC intercalation from solution into swellable silicate films. The influence of the properties of the inorganic component on the structure and optical properties of the intercalated phases of PIC cations was investigated in detail.

2. Experimental methods

Two synthetic layered silicates, fluorohectorite (Corning, Inc., USA) [5] and Laponite RDS (Laporte, Ltd.) [34], and commercially available Kunipia F montmorillonite of natural origin (Kunimine Industries, Japan) [35] were used in the form as received without any purification and pretreatment. Cation exchange capacities (CEC) of the layered silicate specimens are listed in Table 1.

Average surface areas available to one monovalent cation (S_{ion}) and the mean distances between the exchangeable cations (d_{ion}) were calculated. Molecular mass (in unified atomic mass units) equivalent to the unit $O_{20}(OH)_4$ (or $O_{20}F_4$) was calculated from structural formulas [36,37] as a sum of all atomic masses multiplied by stoichiometric coefficients. This value is equal to the mass of 1 mol of structural units (6.022×10^{23}) expressed in $\text{g}\,\text{mol}^{-1}$ (M_{unit}). The surface area S was calculated from

$$S = \frac{N_A \cdot a \cdot b}{M_{\text{unit}}}, \tag{1}$$

where N_A and a and b represent the Avogadro constant ($6.022 \times 10^{23}\ \text{mol}^{-1}$) and the parameters of unit cell dimensions 0.51 and 0.90 nm (0.53 and 0.93 nm for trioctahedral smectites), respectively. The theoretical surface area was used for the calculation of area per monovalent cation according to

$$S_{\text{ion}} = \frac{S}{\text{CEC} \cdot N_A}, \tag{2}$$

where CEC represents the cation-exchange capacity in moles per gram considering the presence of monovalent cations (Table 1).

The films were prepared on fused silica slides transparent in an ultraviolet–visible (UV–vis) spectral range. The slides had been cleaned in a NaOH water/ethanol (10/90 v/v) solution, followed by washing in water and dilute H_2SO_4 aqueous solution. Clean slides were then washed in highly pure deionized water. Aqueous suspensions of layered silicates (0.5% w/w), prepared using ultrasonic bath treatment (20 min), were deposited on the slides using a spin-coating method. The slides with thin films of the silicates were dried in air and directly used for the dye intercalation. PIC was dissolved in high-purity deionized water to obtain the final dye concentration of 1 $\text{mmol}\,\text{dm}^{-3}$. Slides with silicate films were immersed in the PIC solution for 3 h and heated at 60 °C. These conditions were suitable for effective intercalation of the dye cations. The dye amount in the solution was in high excess with respect to the adsorption capacities of the silicates and had not been significantly changed during the intercalation. The excess dye solution was removed by multiple washings with water until no free or reversibly adsorbed dye was released. The films were then dried in air.

UV–vis spectra were measured by a V-550 UV–vis spectrophotometer (Jasco Co., Ltd.) at room temperature. Linearly polarized UV–vis spectroscopy was applied to characterize the molecular orientation of the dye cations. A Jasco polarizer was used for recording the spectra using both horizontally (x-axis direction) and vertically polarized light (y-axis direction). The slide orientation was changed around the x-axis at angles α with respect to the y-axis only. More details on the theoretical background and measurement setup have been published elsewhere [19,38,39]. The basic scheme is described in SI (No. 2). The fluorescence spectra of identical PIC/silicate films were measured using a Shimazu RF5300PC spectrofluorometer. Both the excitation and the emission spectra were measured. The measurement conditions such as wavelengths of light used for the excitation or wavelengths whose intensities were measured are introduced in the text below. The XRD measurements of the identical films were recorded at room temperature for the range of low angles of 2θ to identify the basal spacing values. A RINT-1200 powder X-ray diffractometer (Rigaku Co., Ltd.) with Ni-filtered Cu$K\alpha$ radiation was used.

3. Results and discussion

3.1. Absorption spectroscopy

Fig. 2 shows absorption spectra of PIC intercalated in the films of layered silicates. The film of K montmorillonite exhibits the largest absorbance values, especially at the highest wavelengths. The strong absorption band is assigned to the transitions associated with J-type molecular assemblies [40,41]. The lower wavelengths' bands are assigned to H-type molecular assemblies and isolated PIC cations. The FH film exhibited relatively the lowest absorption in a J-band region.

The J-band position was only slightly dependent on the silicate template used. Analysis of second derivative spectra (see SI, No. 3) showed slightly decreasing energy of maximal absorption in the order of L (570 nm), FH (571 nm), and K (572 nm). These values are a few nanometers lower, if taken directly from the absorption spectra (Fig. 2) (L, 568 nm; FH, 565 nm; K, 571 nm), which