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Uni-Directional Orientation of Cyanine Dye Aggregates on a $K_4Nb_6O_{17}$ Single Crystal: Toward Novel Supramolecular Assemblies with Three-Dimensional Anisotropy

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Organized molecular assemblies with defined geometry are of great interest from scientific and technological viewpoints. Such systems have been constructed by "crystal engineering" through molecular design[1] as well as by immobilization of molecular components on matrices. Immobilization of an organic molecule within low-dimensional inorganic framework is a promising methodology.[2−4] Among possible inorganic matrices, layered materials are advantageous to fabricate multilayered structures, "intercalation compounds", with expandable interlayer distance. Oriented thin films of layered materials were constructed to exploit the anisotropic nature and to use the intercalation compounds as optical and electronic devices.[5−7] However, there remains difficulty to control in-plane orientation of the components.

Here we take advantage of the in-plane anisotropy of $K_4Nb_6O_{17}$[8−10] (Figure 1a) to construct supramolecular structures with three-dimensional anisotropy. Cyanine dyes (Scheme 1) were adsorbed on single crystals of $K_4Nb_6O_{17}$, and the orientations of the dyes were revealed by polarized spectra (Figure 2). Cyanine dyes were used as a probe to examine the orientation and the aggregation, since the dyes form low-dimensional aggregates whose arrangements, for example J-, H-, and herringbone aggregates, and orientations are identified by polarized UV−vis spectra.[11]

Single crystals of $K_4Nb_6O_{17}$ were grown by a flux-method reported previously.[8,9] The crystal was cleaved along the *ac*-plane and cut along *a*- and *c*-axes[9] into platelike rectangular solids with the size of several mm^2 and the thickness of ca. 0.1 mm (Figure 1b). The crystals were allowed to react with solutions of the dyes (water or 1:1 mixture of water and ethanol) for several days at 60 °C and were subsequently washed with acetone or ethanol. Although many cracks stemmed on the crystals after the reactions, the rectangular shapes of the host crystals were retained so that crystallographic directions were refined by XRD analysis from two orthogonal edges.

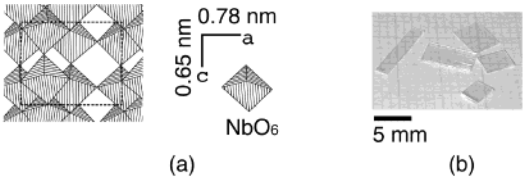


Figure 1. (a) The surface structure of $K_4Nb_6O_{17}$ cleaved from interlayer I and (b) photograph of single crystals of $K_4Nb_6O_{17}$.

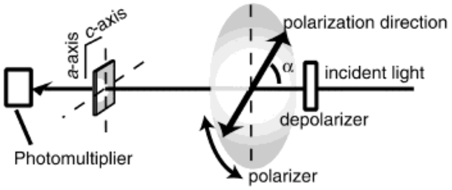


Figure 2. Experimental setup for polarized absorption spectroscopic measurement. Colored sample was fixed in the sample chamber, while the polarizer was rotated so that α, the angle between the fixed *c*-axis of the crystal and the polarized direction of the incident light, was varied.

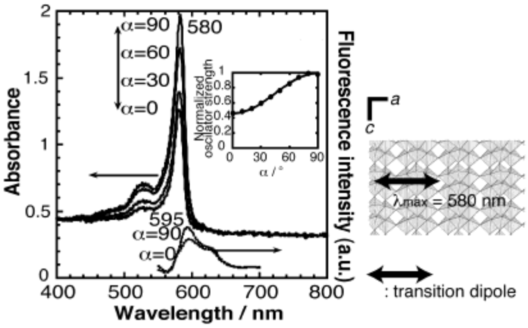
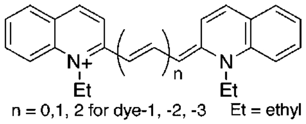


Figure 3. Polarized absorption (solid lines) and fluorescence (dotted lines) spectra of **dye-1** adsorbed on $K_4Nb_6O_{17}$. The inset represents normalized variation of oscillator strength at α. The solid line is the theoretical curve. Orientation of the transition dipole of the dye on $K_4Nb_6O_{17}$ is shown beside the spectra.

Scheme 1. Dyes Used in This Study



The polarized absorption spectra of **dye-1** adsorbed on $K_4Nb_6O_{17}$ are shown in Figure 3, where α represents the angle between the polarization direction and the *c*-axis of the crystal. The absorption bands were centered at around 580 nm, which is red-shifted from that of the monomer band at 525 nm observed in a dilute aqueous solution of **dye-1**. In the fluorescence spectra (Figure 3, dotted line), the fluorescence bands were centered at 595 nm. The spectroscopic observations indicate that **dye-1** form J-aggregates.[11] The monomer bands were absent in the spectra, indicating that most of **dye-1** were present as *J*-aggregates.

The absorbance and the fluorescence intensity varied depending on α, while the wavelengths of the absorption maxima were almost constant. The oscillator strength at $\alpha (f_\alpha)$ was calculated

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by integrating the polarized spectrum at α over energy after removing background. Normalized variation of f_α with α is shown in the inset of Figure 3. Supposing that the dipoles of the *J*-aggregate were preferentially oriented along $\alpha = 90$, f_α is expressed by $f_\alpha = (f_{90} - f_0) \sin^2\alpha + f_0$. The plot in Figure 3 coincided with the theoretical curve (solid line in the figure). The dipoles of the *J*-aggregates is parallel to the long axis of the dye cations.[12] Thus, it was revealed that the dipoles of the *J*-aggregates and the long axis of the dye cations were oriented preferentially, although not perfectly, along the *a*-axis of $Nb_6O_{17}{}^{4-}$ sheets (Figure 3). The difference of the fluorescence intensities at $\alpha = 0$ and $\alpha = 90$ was smaller than the difference in the absorbance. This incompatibility is due to (1) the difference in the experimental setup and (2) the more complicated process for fluorescence. The present system with well-defined geometry is preferable for detailed studies on photophysics of dye aggregates using polarized light.[13]

It seems that the dye aggregates not only on the external surfaces but also in the interlayer spaces, although no remarkable change was found in the XRD patterns after the reactions in any present samples. We have reported the formation of dye aggregates in the interlayer spaces of clays.[14] Adsorption of the dye aggregate in the interlayer spaces in the present system is plausible since (1) the basal spacing was expanded when microcrystalline $K_4Nb_6O_{17}$ was reacted with the dye[15] and (2) every piece obtained by slicing the colored samples along *ac*-plane, was similarly colored.

The adsorbed amount of dye-1 was roughly estimated from the absorbance in the UV−vis spectra (A = up to 2), molar extinction coefficient of the *J*-aggregate ($\epsilon = 2.6 \times 10^4$ mol^{-1} m^2),[12] the volume per 1 mol of $K_4Nb_6O_{17}$ ($V = 2.5 \times 10^{-4}$ m^3 mol^{-1})[10] and the thickness of the sample (L = ca. 1×10^{-4} m). The amount ($=VA/\epsilon/L$) was estimated to be up to 2×10^{-4} molecules per the unit cell of $K_4Nb_6O_{17}$. Because the amount is so small and the PICBr salt on the surface was washed off, it is plausible that the dye cations were adsorbed as a monolayer on the niobate sheet, rather than as PICBr salt. Optical microscopic observation showed that the dye adsorption proceeded from edges and cracks so that the adsorption was inhomogeneous.

Anisotropic absorption spectra were also observed when **dye-2** and **dye-3** were employed. The polarized spectra of the **dye-2** system are shown in Figure 4a. At $\alpha = 0$, the absorption bands were observed at 648 and 604 nm. These bands were red-shifted relative to the monomer band (600 nm). At $\alpha = 90$, these bands were replaced by a new band at 502 nm.

The polarized spectra of the **dye-3** system are shown in Figure 4b. It is remarkable that the orientation direction in the **dye-3** system is rotated by 90° compared to the **dye-2** system, although the spectra resemble to those of the **dye-2** system. At $\alpha = 90$, the absorption band was observed at 835 nm, which was red-shifted from the monomer band of this dye (700 nm). As α decreases, this band gradually disappeared and a blue-shifted band emerged at 618 nm.

Possible interpretation for the spectra is the formation of herringbone-type aggregates with the stacking column direction parallel to the *a*- and *c*-axes for dye-2 and dye-3, respectively. On the basis of extended molecular exciton theory, herringbone-type aggregates show so-called "Davydov splitting".[16,17] This is identified by the absorption bands which are red- and blue-shifted relative to a monomer band and are polarized perpendicularly to each other, as observed in the present dye-2 and dye-3 systems.

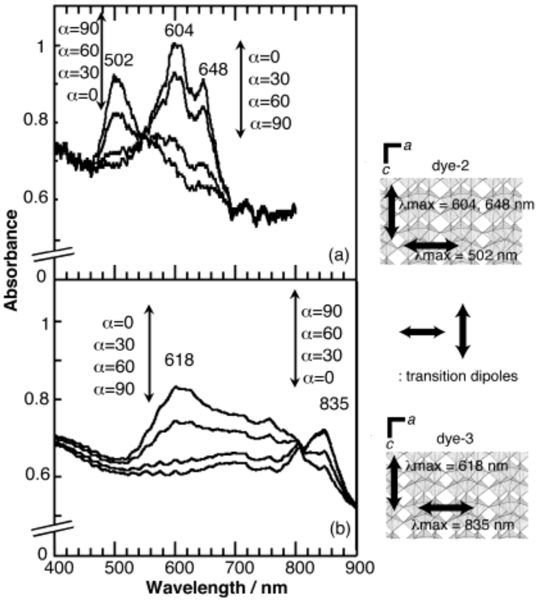

Figure 4. Polarized absorption spectra of (a) dye-2 and (b) dye-3 adsorbed on $K_4Nb_6O_{17}$. Orientations of the transition dipoles of the dyes on $K_4Nb_6O_{17}$ are shown beside the spectra. The spectra (b) were obtained after smoothing calculation.

The dichroism (red/colorless, blue/red, and green/colorless for **dye-1**, **dye-2**, and **dye-3**, respectively) of the samples were observed by naked-eyes under polarized illuminations. Together with the spectroscopic results, it was evident that the aggregates of the cyanine dyes were oriented along crystallographic axes of $K_4Nb_6O_{17}$ over the whole crystal domain.

$K_4Nb_6O_{17}$ have an anisotropic surface (Figure 1a) with regularly arranged NbO^- groups which can act as cation-exchange sites. The electrostatic interactions between the anionic sites and the positive charges on the dye cations should be responsible to the uni-directional orientation of the dye aggregates. Although the mechanism may be similar to those claimed in the reports on epitaxial growth of dye aggregates on AgBr[18] and mica,[19] the surface of $K_4Nb_6O_{17}$ is 1-fold symmetric and anionic unlike those cases. It is possible that the periodic distance of the anionic sites matched (1) with the distance between the localized positive charges on the odd methin carbon of the dye cation[20,21] or (2) with the distance between adjacent dyes induced by cooperation of adsorption with aggregation since the microstructures of the aggregates are strongly directed by dye−dye interaction. Systematic studies with various guests and hosts and detailed spectroscopic characterization will clarify the mechanism further.

Optical properties of dye aggregates are of great interest as model systems of low-dimensional excitons, which bring about useful optical properties.[11,22] The present success in uni-directional control of the dye orientation inside the matrix may lead to future three-dimensional supramolecular devices.

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