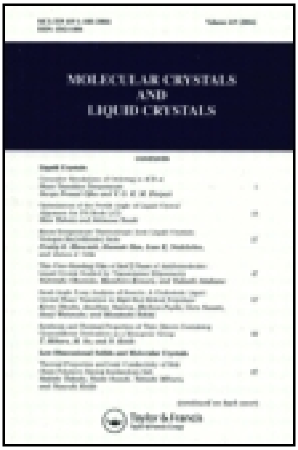

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

# Aggregation of a Cationic Cyanine Dye Intercalated in the Interlayer Space of a Layered Titanate $Na_2Ti_3O_7$

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To cite this article: Nobuyoshi Miyamoto, Kazuyuki Kuroda & Makoto Ogawa (2000): Aggregation of a Cationic Cyanine Dye Intercalated in the Interlayer Space of a Layered Titanate $Na_2Ti_3O_7$ , Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 341:2, 259-264

To link to this article: http://dx.doi.org/10.1080/10587250008026150

*Mol. Cryst. and Liq. Cryst.*, 2000, Vol. 341, pp. 259-264
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Printed in Malaysia

# Aggregation of a Cationic Cyanine Dye Intercalated in the Interlayer Space of a Layered Titanate $Na_2Ti_3O_7$

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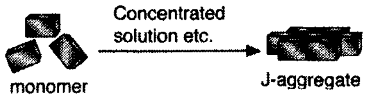
*(In final form July 21, 1999)*

A cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine (PIC), was successfully intercalated into $Na_2Ti_3O_7$ by a guest-exchange method using a propylamine/$Ti_3O_7$ intercalation compound as the intermediate. Based on the XRD and chemical analytical results, it was presumed that PIC was densely packed in the interlayer space with the short axis of its quinoline-ring almost perpendicular to the host layer. Spectroscopic results revealed that the PIC formed J-aggregates even in the restricted space between the titanate layers.

*Keywords:* layered titanates; pseudoisocyanine; J-aggregate

## INTRODUCTION

Cyanine dyes form specific aggregates such as H- and J-aggregates under certain conditions (Scheme 1). J-aggregates of cyanine dyes have attracted much attention for their useful optical properties[1] and for the application as photosensitizers of photographic processes,[2] photoelectric cells and



SCHEME 1 Schematic representation of J-aggregation

photocatalysts consisting of semiconducting materials such as $SnO_2$ and $TiO_2$.[3, 4]

Novel photofunctional materials have been synthesized utilizing restricted nanospaces of layered materials as organizing media of photoactive species.[5] Among possible host materials, layered titanates are host materials with semiconducting properties, which is applicable, for example, to photocatalysts[6]. Intercalation of alkylamines[7] and several photoactive species[8-11] have been conducted. Electron transfer from methylviologen to host layers in the intercalation compounds has been reported.[11]

We have studied the intercalation of a cationic cyanine dye, 1,1'-diethyl-2,2'-cyanine (pseudoisocyanine; abbreviated as PIC; Figure 1), into clay minerals.[12, 13] Aggregation of the PIC was controlled by the nature of clay minerals as well as solvents and coadsorbing species. In the present study PIC was successfully intercalated into $Na_2Ti_3O_7$ by a guest-exchange method using a propylamine/$Ti_3O_7$ intercalation compound as the intermediate. The states of the adsorbed PIC in the interlayer space were discussed on the basis of the XRD and spectroscopic results.

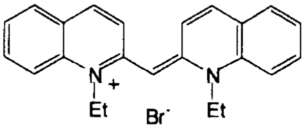


FIGURE 1 1,1'-diethyl-2,2'-cyanine bromide

## EXPERIMENTAL

$Na_2Ti_3O_7$ was synthesized by calcining a mixture of $Na_2CO_3$ and $TiO_2$ (in anatase form) in a molar ratio of 1.1 : 3 at 900 °C for 24 h. Acid treatment of $Na_2Ti_3O_7$ with 1N HCl for 3 days yielded a $H^+$-exchanged form ($H/Ti_3O_7$). A propylamine (PA)-exchanged titanate ($PA/Ti_3O_7$) was obtained by the reaction of $H/Ti_3O_7$ with an aqueous solution of methylamine (40 %) and subsequently with aqueous solution of propylamine (PA) (50%) at 60 °C for 6 days in glass ampoules. Intercalation of PIC was conducted by the reaction of PA/$Ti_3O_7$ with aqueous solutions of PICBr at 60 °C for 6 days in ampoules. The samples were washed with acetone or water. The products were characterized by XRD, IR spectroscopy, elemental analysis and UV-Vis absorption and fluorescence spectroscopies.

## RESULTS AND DISCUSSION

The XRD patterns of the host material and the products are shown in Figure 2. The XRD patterns of $Na_2Ti_3O_7$, and H/$Ti_3O_7$, were in accordance with the reported data.[7, 14] The basal spacing was 0.79 nm for H/$Ti_3O_7$ and was increased to 1.03 nm and 1.28 nm after the reactions with MA and PA, respectively. The reaction of H/$Ti_3O_7$ with MA proceeded almost completely. On the other hand, direct reaction of H/$Ti_3O_7$ with PA resulted in the remaining H/$Ti_3O_7$ phase even when the reactions were prolonged to 3 weeks or repeated. The difference in $pK_b$ values between the organoamines can be a factor to determine the reactivity because the reactions of H/$Ti_3O_7$ with organoamines proceed in terms of the acid-base reaction. However, the $pK_b$ values are not considerably different ($4.5 \times 10^{-4}$ and $4.1 \times 10^{-4}$ for MA and PA, respectively), so it is probable that smaller MA could

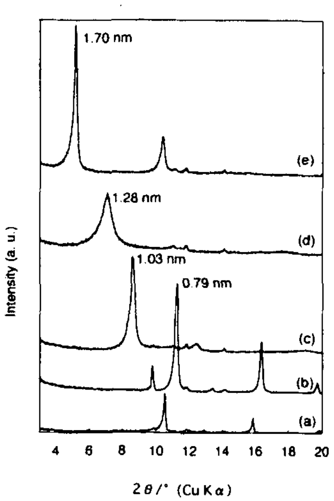


FIGURE 2 XRD patterns of (a) $Na_2Ti_3O_7$, (b) H/$Ti_3O_7$, (c) MA/$Ti_3O_7$, (d) PA/$Ti_3O_7$ and (e) PIC/$Ti_3O_7$.

more easily penetrate into the interlayer space than PA. Finally, PA/$Ti_3O_7$ containing no H/$Ti_3O_7$ phase was obtained by the reaction of the presynthesized MA/$Ti_3O_7$ with PA. The IR spectrum of PA/$Ti_3O_7$ exhibited the absorption bands due to PA and 0.56 mol of PA per $[Ti_3O_7]^{2-}$ was detected by elemental analysis.

Intercalation of PIC was not successful when $Na_2Ti_3O_7$, H/$Ti_3O_7$ or MA/$Ti_3O_7$ was reacted with a PICBr aqueous solution. The XRD patterns after the reactions were similar to those before the reactions. It is probable that large PIC cations could not penetrate into the interlayers. The XRD pattern of the product obtained by the reaction of PA/$Ti_3O_7$ with an aqueous solution of PICBr (PIC/$Ti_3O_7$) exhibited a diffraction peak at d=1.70 nm, which was increased from the value (1.28 nm) of PA/$Ti_3O_7$, indicating the intercalation of PIC. By elemental analysis, 20.9 and 2.2 mass % of C and N were detected in the product. The C/N ratio agrees with that of PIC and the PIC content in the product is estimated to be 0.26 mol per 1 mol of $[Ti_3O_7]^{2-}$, which is supposed to be the maximum amount. Even in the cases that the loading amount of PIC was increased to be 1.20 mol per 1 mol of $[Ti_3O_7]^{2-}$ and that the reaction was repeated, the amount of the adsorbed PIC was 0.26 mol per 1 mol of $[Ti_3O_7]^{2-}$.

The gallery height of PIC/$Ti_3O_7$ is estimated to be 0.91 nm by subtracting the basal spacing of H/$Ti_3O_7$ from that of PIC/$Ti_3O_7$. The size of the molecular plane of PIC cation, which is almost parallel to the quinoline rings of PIC, is 1.50 nm x 0.76 nm and the thickness of the PIC cation is 0.44 nm. Taking the gallery height and the size of the PIC cation into account, two possible orientations of the cations in the interlayer space are conceivable; one is a single layer adsorption with the short axis of the molecular plane almost perpendicular to the host layer and the other is a double layer adsorption with the molecular plain parallel to the host layer. Based on the crystallographic data,[14] the surface area is calculated to be 0.17 $nm^2$ per an unit of $Ti_3O_7$. Assuming the former and the latter types of adsorption of PIC cation, a PIC cation occupies 0.66 $nm^2$ and 1.14 $nm^2$, respectively, and the maximum amount of PIC is calculated to be 0.26 and 0.30 mol per 1 mol of $[Ti_3O_7]^{2-}$, respectively. These values, especially the former one, agree with the experimental result.

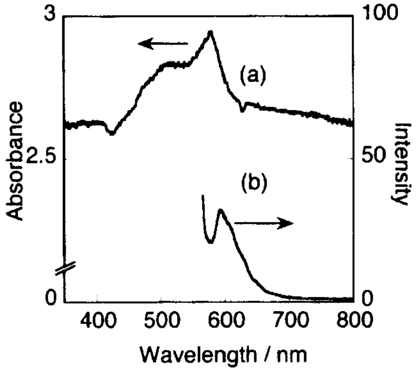


FIGURE 3 (a) Absorption and (b) fluorescence emission spectra (excitation wavelength is 550 nm) of $PIC/Ti_3O_7$ suspended in water.

The absorption and fluorescence spectra of an aqueous suspension of $PIC/Ti_3O_7$ are shown in Figure 3. The absorption spectrum shows an absorption band at around 580 nm which is considerably red-shifted from the monomer band observed for a PICBr aqueous solution at 525 nm. In the fluorescence spectrum, the band, which was not observed in the spectrum of a PICBr aqueous solution, appeared at around 593 nm. These absorption and fluorescence bands are characteristic to J-aggregates of PIC.[15] Due to the excitonic state of J-aggregates, a sharp absorption band and a resonant fluorescence with a small Stokes shift appears. Thus, the PIC formed a J-aggregate even in the restricted space between the titanate layers.

Taking the spectroscopic results into consideration, we assume a single layer adsorption of PIC in the interlayer space with the short axis of PIC quinoline-ring perpendicular to the host layer. In the two dimensionally restricted space between the host layers, this is the only possible packing of PIC to form J-aggregate, which has a two dimensional structure with a face-to-face stacking of the dye cations.[16]

## CONCLUSION

PIC was successfully intercalated into $Na_2Ti_3O_7$ by the guest-exchange method using a propylamine/$Ti_3O_7$ intercalation compound as the intermediate. The intercalated PIC formed J-aggregate even in the restricted space between the titanate layers. It was supposed that the PIC cations were packed densely in the interlayer space with the short axis of its quinoline-ring perpendicular to the host layer. Intercalation compounds of cyanine dyes with layered titanates are worth investigating as a model system of supramolecular photosensitization of nanostructured titanium oxides.

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