



Adsorption and photochemical behaviors of the novel cationic xanthene derivative on the clay surface



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ABSTRACT

Novel tetra-cationic xanthene derivative (Flu) was synthesized. Its adsorption and photochemical behaviors on the clay surface were investigated. Fluorescence quantum yield (ϕ_f) and fluorescence lifetime were 0.50 and 2.9 ns for Flu/clay complex. ϕ_f of Flu was enough high (>0.1) even at high density conditions (0.080 molecules nm^{-2}). It is supposed that the strong interaction between clay and Flu by the 'Size-Matching Effect' realizes the highly emissive clay complexes at high density adsorption condition by a suppression of a molecular aggregation, which tends to decrease the photochemical activity.

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Introduction

We expect that clay minerals can act as one of the ideal host materials to construct structures of dye assemblies for efficient photochemical reactions. Clay minerals are inorganic materials that have negatively charged sites on the flat surface.^{1–4} Photochemical behaviors of organic dyes/clay complexes have been examined by several groups.^{1–16,19–25} Although some unique photochemical properties and reactions were reported,^{1–16,19–25} the photo-activity of dyes on the clay surface tends to be low due to their aggregation behavior. On the other hand, we have successfully prepared unique porphyrin/clay complexes in which the porphyrin molecules adsorb on the clay surface without an aggregation even at high dye loadings.^{2,4,7–16} This non-aggregation behavior takes place when the distance between intramolecular cations of dyes matches well with it between negatively charged sites on the clay surface. We named this effect as the 'Size-Matching Effect'.^{2,4,7–16} By using this unique phenomenon, we have reported efficient energy transfer systems aiming an artificial light harvesting.^{12–16} Recently, we have examined various organic dyes other than porphyrins as a guest dye. Among them, we found out that xanthene derivatives exhibit unique adsorption and photochemical behaviors on the clay surface. Xanthene dyes such as fluoresceins, eosins, fluorones, and rhodamines are useful dyes as

fluorescent probes and a dye for a dye laser.^{17,18} They have a high fluorescence quantum yield and an enough long fluorescence lifetime as photo-functional dyes. Although fluorescent rhodamine–clay complex has been investigated,^{5,19–25} rhodamine molecule easily forms their aggregates on the clay surface at high dye loadings.^{19–21,25} Some researches dilute the dye molecules by surfactants and succeeded to suppress the aggregation of rhodamine dyes in the clay complex. Such complexes exhibit highly emissive properties (fluorescence quantum yield; $\phi_f \sim 0.8$).^{22,23} On the other hand, the adsorption density of dyes on the clay surface was not so high^{22,23} ($0.00094\sim 0.0031$ molecules nm^{-2}) because of a dilution with surfactants. In this study, we designed and synthesized the novel tetra cationic xanthene dye (Flu) and investigated its adsorption and photochemical behavior with and without clay in water. As a result, we obtained the xanthene–clay complex where an aggregation behavior was not observed even at high density conditions and ϕ_f is enough high ($\phi_f \geq 0.1$) at relatively high density conditions (0.080 molecules nm^{-2}) without any diluting reagent such as surfactants.

Experimental section

Materials

p-2,4,5,7-Tetrakis(*N*-methylpyridinium-4-yl)-6-potassiumoxy-3-fluorone (Flu, Fig. 1) was synthesized as shown in [Supplementary materials](#). Water was deionized with an ORGANO BB-5A

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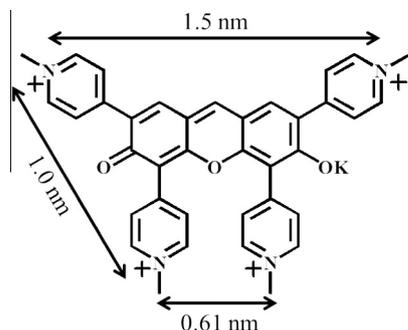


Figure 1. The structure of *p*-2,4,5,7-tetrakis(*N*-methyl pyridinium-4-yl)-6-potassiumoxy-3-fluorone (Flu). The inter-cationic distance calculated by the PM6 method is shown by arrows.

system (PF filter $\times 2 + G-10$ column). The saponite clay used in this experiment was Sumecton SA (SSA), which was received from Kunimine Industries Co. Ltd. The stoichiometric formula is $[(\text{Si}_{7.20}\text{Al}_{0.80})(\text{Mg}_{5.97}\text{Al}_{0.03})\text{O}_{20}(\text{OH})_4]^{-0.77} (\text{Na}_{0.49}\text{Mg}_{0.14})^{+0.77}$, the surface area is $750 \text{ m}^2 \text{ g}^{-1}$, and the cationic exchange capacity (CEC) is $99.7 \text{ meq}/100 \text{ g}$. On the basis of these values, the average area per anionic site is calculated to be 1.25 nm^2 , and thus the average distance between anionic sites on the clay surface is estimated to be 1.2 nm , on the basis of the assumption of a hexagonal array. The SSA was used after purification.

Purification of clay

SSA (2.1 g) was dispersed into water (200 ml), and the colloidal solution stood for 9 days. Then, the supernatant liquid (150 ml) was decanted, and SSA was separated by centrifugation (18,000 rpm, 10 h, 10°C). The supernatant was removed and deionized water was added to it. After standing for 1 day, SSA was separated by centrifugation (18,000 rpm, 5 h, 10°C) again. The supernatant was removed, and SSA was collected by filtration with PTFE membrane ($0.45 \mu\text{m}$, Millipore) (1.0 g, yield 48%).

Analysis

Absorption spectra were measured with Shimadzu UV-3150 spectrophotometer. The corrected fluorescence spectra were measured with Jasco FP-6500 spectrofluorometer. In absorption measurements, a quartz cell was used for aqueous clay/dye solution. In fluorescence measurements, a plastic cell (PMMA) was used for aqueous clay/dye solutions. TG/DTA measurements were carried out with a Shimadzu DTG-60H analyzer to determine the water content of the dyes and clay. According to TG measurement, the water content of SSA and Flu was determined to be 12.7% and 7.0%, respectively. Molecular weight of SSA and Flu was corrected according to the water content. X-ray Fluorescence (XRF) was observed with Rigaku ZSX 100E under vacuum. The fluorescence lifetime was measured by a Hamamatsu Photonics C4780 ps fluorescence lifetime measurement system. The excitation light source of the C4780 was a laser diode (406 nm, 71 ps fwhm, 1 kHz). The laser flux was reduced with neutral density filters to avoid nonlinear effects.

Preparation methods for the clay/dye complexes

Preparation for Flu/clay complex for Lambert–Beer plot

Absorption spectra of Flu/clay complexes were observed as described below. Flu/clay complex was typically prepared by mixing of the aqueous clay solution and the respective aqueous Flu solution under stirring. The dye loadings were changed by adjusting the concentration of Flu. The concentration of clay was always kept constant at 4.0 mg L^{-1} .

Preparation for Flu/clay complex for fluorescence spectra

Fluorescence spectra of Flu/clay complexes were observed as described below. Flu/clay complex was typically prepared by mixing of the aqueous clay solution and the respective aqueous Flu solution under stirring. The clay loadings were changed by adjusting the concentration of clay. The concentration of dye was always kept constant at $1.0 \times 10^{-1} \mu\text{mol L}^{-1}$.

Under these conditions, the clay sheets exist in a form of individually exfoliated sheets and the obtained solution was substantially transparent in UV-vis. region.

Preparation for Flu/clay complex for measuring XRF

The Flu/clay complex was made as film for measuring XRF. The film was prepared as shown in [Supplementary materials](#).

Results and discussion

Adsorption behavior of Flu on the clay surface

Absorption spectra and fluorescence spectra of Flu without clay are shown in [Figure S2](#). The absorption and fluorescence maxima are 525 and 565 nm, respectively. The absorption coefficient of Flu at 525 nm is $9.14 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$. Adsorption behavior of Flu on the clay surface was examined by the measurement of absorption spectra. Absorption spectra of Flu on the clay surface were observed at various dye loadings (10–260% vs CEC) as shown in [Figure 2](#). While the spectra retained same shape below 140% versus CEC adsorption, the observed spectral shape changed above 140%. This indicates that the new species appeared above 140% versus CEC adsorption. The λ_{max} (525 nm) and the spectral shape of new species above 140% are same as that of Flu in water without clay. Thus, the long-wavelength absorption at 553 nm was the component of the adsorbed Flu on the clay surface, and newly superimposed short-wavelength absorption at 525 nm was a component of non-adsorbed Flu in bulk solution. All spectra can be expressed by the combination of the component of the adsorbed Flu on the clay surface and it of the non-adsorbed Flu. This type of spectral shift to longer wavelength (532 \rightarrow 553 nm) upon the complex formation with clay is frequently observed for aromatic compounds. According to the literature,¹⁰ the λ_{max} shift of Flu upon adsorption on the clay surface is due to the expansion of conjugated system by the planarization of the molecular structure on the clay surface.⁴

The Lambert–Beer plot for Flu/clay complexes at 525 and 553 nm is shown in [Figure 3](#). As shown in [Figure 3](#), the linearity of the plot was observed below 134% versus CEC of the clay. Thus, it turns out that the Flu does not form aggregate in the ground state

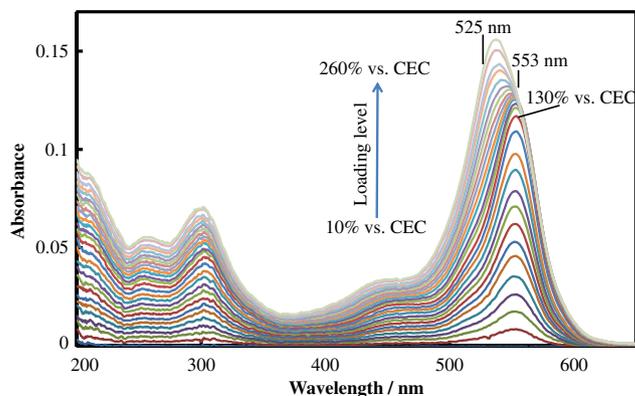


Figure 2. Absorption spectra of Flu/clay complexes at various concentrations of Flu. The loading levels were 10–260% versus CEC of the clay at intervals at 10% versus CEC in water. The concentration of clay was 4.0 mg L^{-1} .

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