

Energy transfer between rhodamine 3B and oxazine 4 in synthetic-saponite dispersions and films

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Abstract

The objective of this study was the investigation of energy transfer between the laser dyes rhodamine 3B (R3B) and oxazine 4 (Ox4) adsorbed on the surface of synthetic Sumection saponite (Sum). The process of energy transfer was studied for both saponite dispersions and oriented solid films. The electronic properties, luminescence, and the energy transfer process were described by UV–vis absorption and fluorescence spectroscopy. For the efficiency of the energy transfer process, the concentrations of energy donor and acceptor components on a clay mineral surface were found to be essential. A side reaction of the molecular assembly formation reduced both the luminescence and energy-transfer yields, mainly due to fluorescence quenching. The quenching was more problematic for the solid film specimens, where an appropriate modification of the inorganic host with hydrophobic alkylammonium cations was used to achieve a higher luminescence. Due to the higher tendency of Ox4 to form nonluminescent aggregates at higher concentrations, the lowering of the Ox4 concentration further improved the luminescent properties of the films. In this case, the energy transfer occurring in the solid film from R3B to Ox4 was clearly proven.

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1. Introduction

Molecular aggregates are self-assembled supramolecular structures of simple molecules, which are held together by electrostatic and/or weak van der Waals forces. The self-organizing nature of such assemblies would be based on the spontaneous stacking or alignment of molecules directed by their geometrical shape and size and contact energies [1]. Molecular assemblies of organic molecules are formed in hybrid organic/inorganic materials, whose structural characteristics can be significantly influenced by an inorganic template. One example is materials that are based on dye supramolecular assemblies called molecular aggregates, which are formed after the intercalation into inorganic host materials. Such materials are of great interest because of their properties [2], and are potential candidates to be novel optical materials [3,4]. There are various methods that can be used for constructing hybrid or-

ganic/inorganic materials, based on inorganic solid hosts, for example, the Langmuir–Blodgett method for the preparation of thin films of organic molecules on an inorganic substrate (e.g., [5]), direct intercalation into an inorganic host (e.g., [2]), in situ formation of inorganic solids with organic molecules (e.g., [6]), and electrostatic layer-by-layer assembly (e.g., [7]).

Clay minerals, such as smectites and related synthetic layered silicates, are suitable hosts for the construction of hybrid organic/inorganic nanomaterials [8]. Due to the isomorphic substitutions in the structure, the smectite layers possess a negative charge. The distribution of the charge is one of the most important characteristics of these materials [9]. The negative charge is compensated by hydrated inorganic cations that can easily be exchanged with organic cations via an ion-exchange reaction. For large organic cations, sufficient interlayer swelling of the host material is required. Expansion of the interlamellar spaces, which can lead to macroscopic swelling, is achieved under appropriate conditions and depends on the solvent and the type of original exchangeable cations as well as the layer charge of smectite [10].

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As mentioned above, the adsorption of organic dye cations is often accompanied by molecular aggregation [11]. Depending on the layer charge, various forms of dye assemblies can be formed, such as dimers and larger molecular aggregates of the H- and J-type. Dye molecular assemblies can easily be distinguished by electron spectroscopy methods [12]. H-aggregates absorb light at higher energies than isolated dye cations and are characterized by sandwich-type intermolecular association. The characteristic feature of the H-aggregates is lack of luminescence and fluorescence quenching of the co-existing luminescent species. On the other hand, J-aggregates, which are characterized by head-to-tail intermolecular association, absorb light of significantly lower energies. In contrast to the H-aggregates, the J-aggregates exhibit luminescence and other interesting properties [12]. Molecular aggregation is often a crucial problem occurring during the preparation of luminescent hybrid materials based on organic dyes and inorganic hosts. However, recently, Sasai et al. [13] managed to prepare highly luminescent films of clay minerals with adsorbed rhodamine 6G. The molecular aggregation of the dye was suppressed due to premodification of the inorganic host with appropriate amounts of long-chain alkylammonium ions.

Xanthene dyes, which include, e.g., rhodamines and oxazines, represent a large group of laser dyes that have been widely used as an optically active part in hybrid organic/inorganic materials. One could mention materials prepared using silica gels [14], glass [15], or more complex polymer-filled microporous glass [16]. Numerous studies have dealt with the interaction of rhodamine dyes with clay minerals in dispersions (e.g., [17]) or in self-assembled films (e.g., [18–21]). Ras et al. [22] studied the molecular organization of rhodamine with hydrophobic octadecyl groups in the molecules in hybrid Langmuir–Blodgett layers also including single-layer coverage by clay mineral particles.

The co-adsorption or intercalation of two structurally different cationic dyes leads to a more complex system. Similarly to the adsorption of a single dye, the adsorption on a clay mineral surface is based on an ion exchange, if both the dye components are cationic. However, one has to consider the chemical and physical interaction between the different dye components. Chemical interactions may include competitive adsorption or the formation of mixed molecular assemblies or potential chemical reactions. Physical interactions between fluorophores include fluorescent resonance energy transfer (FRET). In FRET, one component acts as an energy donor and, upon excitation, transfers energy to the second dye molecule, an energy acceptor, which is in the vicinity of the donor one. The transfer proceeds in a nonradiative way, via a long-range dipole–dipole coupling mechanism [23]. FRET requires a suitable combination of electronic properties of the components. Spectral overlap between the emission and excitation spectra of energy of the donor and acceptor components, respectively, is a basic condition for FRET to occur. The efficiency of the energy transfer depends on the distances and orientation of the interacting molecules. The energy transfer is frequently used as an analytic technique in various fields of biochemistry and molecular biology for investigations of intermolecular interactions [24–26].

Energy transfer does not normally take place in dilute dye solutions due to the large distances between molecules. The objective of our work was to optimize the conditions for energy transfer between dye cations after their concentration on a clay mineral surface. The adsorption of two laser dyes, namely rhodamine 3B (R3B) and oxazine 4 (Ox4), on microscopic particles of the synthetic Sumecton saponite (Sum) was investigated. The energy transfer process was studied for both aqueous dispersions and thin films of the saponite.

2. Experimental

2.1. Materials

A synthetic saponite, Sumecton SA, (Sum) from the Kunimine Ind. Co. was used in this study. The cation exchange capacity of Sum is $0.87 \pm 0.05 \text{ mmol g}^{-1}$ [27]. The cationic laser dyes rhodamine 3B (R3B) and oxazine 4 (Ox4) were purchased from Lambda Physik GmbH (Göttingen, Germany) and used without further purification. The molecular structures of the R3B and Ox4 cations are shown in Fig. 1. Dodecyltrimethylammonium bromide (DTMA) from Aldrich was used as received.

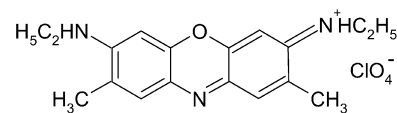
2.2. Preparation of dye(s)/saponite dispersions

The final dispersions were obtained by mixing the Sum dispersion and mixed dye solutions containing both the R3B and Ox4. The final concentration and loading of the dye solutions in the dispersions were always $1 \times 10^{-6} \text{ M}$ and 0.05 mmol g^{-1} of smectite, respectively. The dyes were quantitatively adsorbed onto saponite particles, which was proven by the absence of the dyes in supernatants obtained by filtering the dye/saponite dispersions.

2.3. Preparation of dye(s)/saponite films

Oriented solid thin films of saponite were prepared by the spin-coating of a 25 mg/5 ml aqueous suspension of Sum on

Ox4



R3B

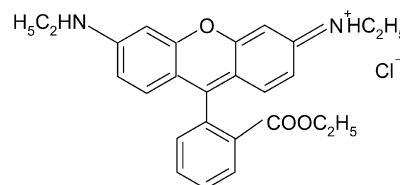


Fig. 1. Molecular structures of Ox4 and R3B.

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