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Fluorescence resonance energy transfer between laser dyes in saponite dispersions

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Abstract

Fluorescence resonance energy transfer (FRET) between two cationic dyes, rhodamine 6G (R6G) and oxazine 4 (Ox4), in smectite (synthetic saponite, Sumecton) dispersions was studied. The interaction between smectite and the dyes was studied using visible (vis) and fluorescence spectroscopies. Only slight differences were observed between the vis spectra recorded in the presence and absence of the smectite. Due to low charge density of the smectite, the dyes did not form molecular aggregates in significant amounts. FRET was absent in the dye mixture solutions, but efficiently proceeded in aqueous dispersions with the smectite. The optimal conditions were observed for the concentration of 10^{-5} M for both dye components. Lower concentrations of each dye probably led to larger intermolecular distances between the adsorbed dye cations, which reduced the efficiency of the energy transfer between the energy donor (R6G) and acceptor (Ox4). On the other hand, higher concentrations were not suitable for the FRET to run efficiently. Probably, self-quenching took place at high concentration of dye cations at interface. Formation of the H-type molecular assemblies with a sandwich-type association, which are very efficient quenchers, was not spectroscopically observed. No influence of the addition of the surfactant was observed in the systems with optimized conditions.

Keywords: Fluorescence resonance energy transfer; Smectite; Laser dyes

1. Introduction

Nanocomposite materials based on laser organic dyes adsorbed onto the surface of inorganic layered compounds are interesting due to their potential applications in photochemistry [1–3]. Smectites are clay minerals and represent one of the most interesting inorganic layered materials. They are composed of microscopic particles of nanometer thickness. Due to the isomorphic substitutions in their structure, smectite layers bear a net negative charge. The negative charge is balanced by hydrated inorganic cations, which can be easily exchanged. The immersion of smectite into a liquid phase, such as aqueous solutions or organic solvents, leads to material swelling. The negative layer charge, ion exchangeability and swelling are some of the most important physical and chemical properties of the smectites. These properties are very important for the intercalation of large-size organic cations, including those of organic dyes [4].

The adsorption of organic dyes on the smectite surface is not a simple process. Besides the adsorption, molecular aggregation of the cationic dyes often occurs [5–9]. This is very important, because the molecular aggregation significantly affects the optical properties of the organic dyes. For example, the formation of H-aggregates, which are molecular assemblies with a sandwich-type association, leads to a significant luminescence quenching [7].

Dye adsorption enhances the concentration of the dye molecules, which may promote their intermolecular physical and chemical interactions. For example, if two molecules of the luminiscent dyes are in close proximity, fluorescent resonance energy transfer may occur. In this process, interacting molecules would represent two components, the energy donor and acceptor. The energy donor molecules initially absorb electromagnetic radiation and are excited. If there was no energy acceptor in the vicinity of these molecules, the energy would

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eventually return back to the ground state via a radiative and/or a non-radiative deactivation processes. When in the vicinity of a donor is a second dye molecule, which is a suitable energy acceptor, the energy transfer can occur. After the transfer of energy, the acceptor molecules become electronically excited, which can be followed by photon emission from the acceptor molecule. In real processes, the transfer of energy leads to the reduction of the donor light emissions and excited lifetimes and to the increase in light emission from the acceptor molecules [10,11]. Non-radiative energy transfer can occur via the Förster dipole–dipole interaction, the so-called fluorescence resonance energy transfer (FRET) mechanism.

There are some basic conditions for FRET to occur. The absorption and emission spectra of the acceptor must overlap the emission spectrum of the donor [12]. Further requests include suitable molecular orientations and short intermolecular distances between the donor and acceptor molecules. In other words, the donor and acceptor must be close to each other; typically between 10 and 100 Å [13]. Considering the proximity of the donor and acceptor molecules, the FRET provides an opportunity to investigate molecular interactions and to estimate the distances between the two molecules.

There are only limited data or knowledge on the FRET occurring in the systems composed from organic dyes and clay minerals [14–19]. Clay minerals play the role of templates, which concentrate the dye molecules (ions) on their surface. In such a way, close interaction between energy donor and acceptor component is possible, in contrast to inactive systems based on homogeneous solutions. A typical example is energy transfer between porphyrin dyes in clay mineral dispersions [14]. The non-aggregated form of porphyrin dyes is easily achieved even in concentrated form due to a flat molecular orientation on the clay mineral surface, influenced mainly by the molecular shape of the dye and presence and distribution of positive charge groups. The phenomenon of energy transfer was proven also for layer-by-layer assemblies of clay mineral, cationic polypeptide polylysine and cyanine dyes [15]. Efficient energy transfer occurred between adjacent layers built from different cyanine dyes. Further examples of energy transfer in clay mineral systems are triplet–triplet energy transfer from bound sensitizers to mircene [16] and to aromatic hydrocarbons adsorbed in hydrophobic organoclay [17]. Probably first records on efficient energy transfer in clay mineral systems, based on the interaction between chemically different dye types, are clay mineral dispersions with cyanine (energy donor) and rhodamine (energy acceptor) dyes simultaneously adsorbed on clay mineral surface [18,19]. Systems with other (non-clay mineral) inorganic solids have more frequently been reported to be suitable and efficient templates for energy transfer between adsorbed chromophores [1,20]. However, low yields of the energy transfer at the interface were often the problem for laser dyes (e.g. rhodamines and oxazines), which are otherwise highly luminescent in the form of dilute solutions. This fact can be likely attributed to enhanced molecular aggregation at interface.

In our study, we used two cationic laser dyes, rhodamine 6G and oxazine 4, representing a suitable energy donor and acceptor, respectively. R6G is a fluorescent dye with a high quantum yield [21]. R6G cations absorb light at 526 nm in dilute solutions. The position of this band in clay dispersions is shifted to a slightly longer wavelength. However, depending on the smectite species used as a template, the R6G cations can form various molecular assemblies at the interface [22]. H-aggregates of the R6G cations absorb light of significantly higher energies. As mentioned above, the formation of these species leads to a significant decrease in the luminescence. Martinez et al. [23] studied in detail the formation of molecular aggregates in rhodamine/smectite systems by measuring the spectral characteristics of the dye, such as spectral shift and band splitting. They interpreted these spectral changes using an exciton theory and the methods of quantum mechanics by considering the electrostatic interactions between the transition moments of the interacting cations. Sasai et al. [24] showed that the R6G molecular aggregation in silicate films can efficiently be minimized and the luminescence of the adsorbed dye molecules be increased in the presence of long-chain cationic surfactants. Besides the H-aggregates, J-aggregates can also be formed at the smectite interface. For some rhodamine dyes, the J-aggregates are commonly formed and, in contrast to the H-ones, are luminiscent. The J-aggregates absorb light of significantly higher wavelengths with respect to the isolated cations and are characterized as molecular assemblies with a head-to-tail intermolecular association [25]. Oxazine 4 (Ox4) is a cationic laser dye of the xanthene type with spectral properties similar to rhodamines. It absorbs light at 615 nm in aqueous solutions, but forms molecular assemblies in concentrated solutions or at interfaces. Chen et al. [26] studied the intercalation of rhodamine 6G and oxazine 4 into oriented taeniolite films. They identified various forms of oxazine 4 including monomers, H-dimer, and H- and J-aggregates, which absorbed light in a very broad range of wavelengths.

R6G and Ox4 are in principle a suitable couple of the dyes for the FRET. The dyes are highly luminescent and the emission spectrum of the R6G sufficiently overlaps with the excitation of Ox4. The objective of this work was to find suitable experimental conditions for the energy transfer from R6G to Ox4 after dye adsorption on smectite particles in dispersion.

2. Experimental methods

2.1. Materials

A synthetic saponite "Sumecton SA" (Sum) from the Kunimine Ind. Co., was used as received. This smectite is a colorless and highly pure specimen, which is easily dispersed in water. The structural formula of Sum is as follows:

$$\mathrm{Na_{0.49}Mg_{0.14}[(Si_{7.20}Al_{0.80})(Mg_{5.97}Al_{0.03})O_{20}(OH)_4]}$$

The cation exchange capacity of Sum is 0.997 meq. g^{-1} [27]. However, our experiments based on the measurements of the methylene blue spectra indicate a very low charge density for this smectite [28]. Indeed, a detailed study confirmed a partially lower CEC of 0.87 ± 0.06 mmol g^{-1} determined with the method using ion exchange with barium chloride solution [28]. Sum does not contain iron in its structure, which otherwise frequently occurs in natural smectites. The presence of this element in the system could lead to a significant quenching of the luminescence. Therefore, the absence of iron might be very important property [29].

Cationic laser dyes, R6G and Ox4 (Lambda Physik GmbH, Göttingen, Germany), were used without further purification. Their properties have been described elsewhere [22–24,26].

2.2. UV–vis measurements

The UV–vis spectra of the R6G/Ox4/smectite dispersions were measured using a UV–vis V-550 spectrophotometer (Jasco Co., Ltd.). The final concentration and loading of the dye solutions in the dispersions were always 10^{-6} M and 0.05 mmol g^{-1} (sums for a mixture of the dyes) of smectite, respectively. The visible spectra were measured 1 min and 24 h after mixing the dye solutions with the clay dispersions. The spectra of the smectite dispersions without dye, related to light scattering, were subtracted from the spectra of the dye/smectite dispersions in order to obtain the pure spectra of the dye species. The positions of the bands were determined by a second derivative spectroscopy.

2.3. Fluorescence measurements

The emission spectra of the R6G/Ox4/clay dispersions were obtained using a Shimadzu RF-5000 spectrofluorometer. The excitation was performed at 500 nm for all the measurements. The excitation wavelength was chosen to only excite the R6G cations. The Ox4 cations do not significantly absorb light at this wavelength. Under these conditions, the occurrence of FRET can be known only by light emission from Ox4 cations.

We tested the effect of the concentrations of Ox4 and R6G. We prepared two series of the dyes/smectite dispersions. In the first case, the initial concentration of Ox4 was kept constant (10^{-5} M) while the concentration of R6G varied (5×10^{-5}, 10^{-5}, 5×10^{-6}, 2×10^{-6}, 10^{-6}, 10^{-7} M). In the second case, the concentration of R6G remained constant (10^{-5} M) and the concentrations of Ox4 were changed (5×10^{-5}, 10^{-5}, 5×10^{-6}, 2×10^{-6}, 10^{-6}, 10^{-7} M). The loading of the Sum was 0.05 mmol g^{-1} in all cases.

3. Results and discussion

3.1. Absorption spectra

Fig. 1 shows the absorption spectra of the cationic dyes R6G and Ox4 and their mixtures in aqueous solution (a) and Sum dispersion (b). The main absorption bands for the R6G and Ox4 aqueous solutions are, at 523 and 614 nm, respectively. Small shoulders, which are detected at the lower wavelengths, are likely 0–1 vibronic components of the electronic transitions, but may also include light absorption of the traces of H-dimers. The absorption spectrum of a 1:1 mixture solution (Fig. 1a, solid line) shows two bands related to the light absorption of the individual components (dashed and dotted lines). In the case of the saponite dispersion, the main bands are shifted to slightly higher wavelengths, 534 and 622 nm, respectively (Fig. 1b). The intensity of the band in the case of the R6G dye is analogous to the aqueous solution; the intensity of the Ox4 band is only slightly higher. Another set of spectra was measured after 24 h (not shown), but no significant changes were detected. This indicates that the dye species, which had been formed after the dye adsorption, were stable and did not change with time.

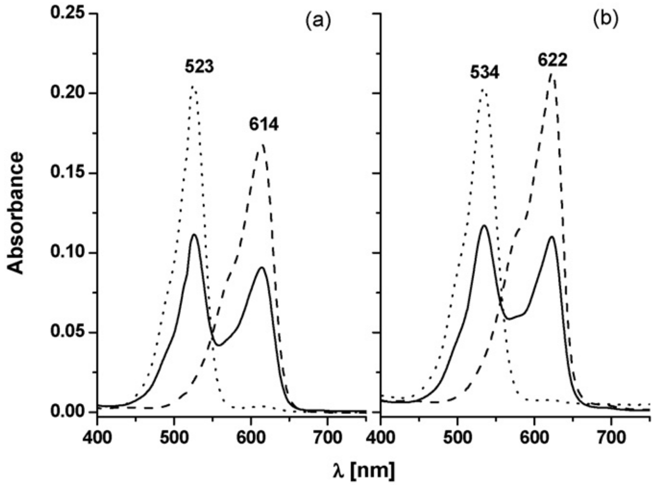

Fig. 1. Absorption spectra of cationic dyes R6G (dotted) and Ox4 (dashed) and their mixtures (solid) in water (a) and in Sum dispersion (b).

The adsorption of cationic dyes in the smectite dispersion is a very fast and rather complex reaction [30]. During the ion-exchange reaction, the aggregation of cationic dyes often occurs, which is controlled by the distribution of the surface charge [31,32]. The absence of the aggregation of both the R6G and Ox4 can be interpreted in terms of the low layer charge density of Sum. Similar trends have been observed during the interaction of this smectite with methylene blue [28]. The absence of significant amounts of H-aggregates of R6G and Ox4 in the Sum dispersions is very important for using this reaction system for realizing fluorescence resonance energy transfer. As already mentioned, the presence of the H-aggregates, either of the energy donor or acceptor type, could lead to a significant quenching of the luminescent properties of the system. The aggregates of the acceptor could take part in the energy transfer process, however, only leading to a fluorescence quenching. In this case, the energy transfer would be observed as a reduction of the donor emission, but without following emission at higher wavelengths from the acceptor molecules.

3.2. Fluorescence spectra

Fig. 2 shows the emission spectra of the cationic dyes, R6G and Ox4, and their mixture in aqueous solution (a) and in the dispersion with Sum (b). The emission spectra were obtained after excitation at 500 nm. As mentioned above, the excitation wavelength was appropriately selected to excite the R6G cations while avoiding or at least minimizing the direct excitation of the Ox4. The maximal emission for the aqueous solution of R6G is located at 552 nm. A negligible emission is observed for Ox4, being at about 630 nm, after the excitation at 500 nm. Hence,

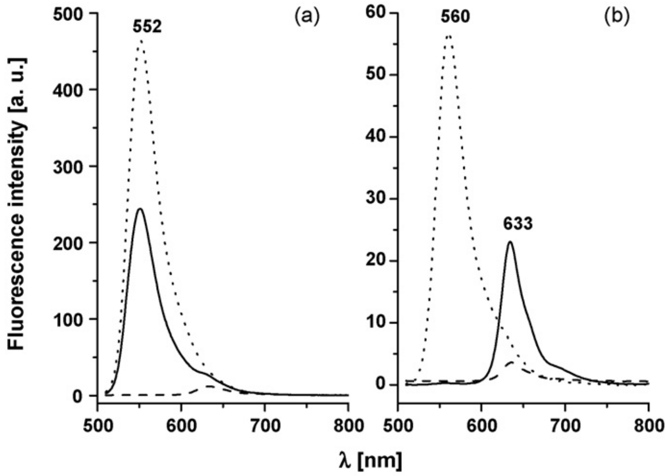

Fig. 2. Emission spectra of cationic dyes R6G (dotted) and Ox4 (dashed) and they mixtures (solid) in water (a) and Sum dispersion (b). Excitation was perfomed at 500 nm. The concentrations of the dyes were 10^{-5} M.

significant emissions from the Ox4 would be possible only after excitation via energy transfer from the R6G cations.

The emission spectrum for the mixture solution is composed of those for the individual components. In other words, no energy transfer occurs in the solution. The energy transfer leads to changes in the emission spectra. The corresponding emission spectra in the Sum dispersion are shown in Fig. 2b. The trends in the emission spectra for the individual dyes in the Sum dispersion are almost analogous to those in the aqueous solution (Fig. 2a). The only changes are related to the slight shifts of the bands to higher energies; 560 and 633 nm, respectively (Fig. 2b). Much greater differences are related to the intensities of the bands. One can see that the emission in the dispersions is significantly reduced (around 10 times) due to the presence of a clay mineral. The reduced luminescence might be potentially explained in terms of light scattering from the smectite particles present in the dispersions. However, measured decrease of the absorbance due to light scattering from clay mineral particles was very low, almost negligible with respect to the light absorbed by R6G. We also do not expect significant scattering of emitted light as well. Another cause is a fluorescence quenching that frequently occurs when dye molecules are adsorbed at interfaces. The quenching is a phenomenon when the energy is transferred from the excited state of monomers to the molecular aggregates of an H-type. López Arbeloa et al. [33] suggested that this process can be via Coulombic interactions (a dipole–dipole type) or an electron exchange mechanism. H-aggregates are not luminescent, and, furthermore, are very efficient quenchers even at extremely low concentrations [33]. However, the H-aggregates were not detectable; hence, it is difficult to judge if trace amounts of the molecular aggregates could quench so efficiently the luminescence from the monomers. Furthermore, quenching of excited dye cations may occur also via mechanism called self-quenching. The self-quenching is characterised by interaction of an excited molecule with another molecular entities of the same species in the ground state. It frequently occurs at the interfaces, when (local) concentration of adsorbed molecules is very high and intermolecular distances are low [34]. One can suppress the dye aggregation or reduce the concentration, thus increasing the intermolecular distance by the co-adsorption of cationic surfactants such as long-chain alkylammonium cations. Therefore the systems composed from clay mineral with adsorbed both dye and alkylammonium cations are typical of superior luminescent properties [35].

The main qualitative changes in the emission spectra occur for the reaction system containing a mixture of cationic dyes in the Sum dispersion. The band at 552 nm completely disappeared in favor of the band at 633 nm (Fig. 2b). In this case, the R6G cations did not emit light, but the energy was transferred from the R6G to Ox4 cations. After the energy transfer, the electrons of the Ox4 ions became excited, which was followed by light emission from the molecules of this dye. One should note that the FRET was achieved in the system with smectite, but was not observed for the system containing only the aqueous solution. In this case, smectite particles played a role in the concentration of the dye cations on their surface. The intermolecular distances between the energy donor and acceptor molecules were suitable for the energy transfer to occur. We tested the effects of other reaction conditions for the preparation of the R6G/Ox4/Sum dispersions on the energy transfer. The conditions included dispersion aging and the preparation conditions. The dispersions were prepared by the addition of the dye mixture to the smectite dispersion (standard procedure) or by adding individual solutions of the dyes in two steps, in which the order of the added components was varied. In all the experiments, final concentrations of the components were the same. Varying the reaction conditions did not lead to significant changes in the spectral properties or energy transfer process (not shown).

In the next step, we studied the effect of the concentration of dyes. In Fig. 3a and b, the emission spectra of the R6G/Ox4/Sum system are shown. In the first series of experiments, the concentration of Ox4 remained constant (10^{-5} M) and the concentrations of R6G decreased from 5×10^{-5} to 1×10^{-7} M. Energy transfer did not occur to a significant extent for the system with the highest R6G concentration of 5×10^{-5} M (Fig. 3a). The spectrum is dominated by the band at 560 nm assigned to an R6G emission. Only part of the energy might have been transferred from R6G to Ox4, which is indicated by the shoulder of low intensity at approximately 630 nm, assigned to the emission from the Ox4 cations. There was a significant excess of R6G cations versus Ox4 ones in this reaction system. The large amount of R6G led to a significant emission from this dye. Although the Ox4 concentration was sufficient, no substantial energy transfer to the Ox4 cations took place. One explanation could be based on the self-quenching by abundant R6G molecules. Quenching by the H-aggregates was not confirmed, since no significant amount of the H-aggregates has been observed under these conditions (not shown). H-type aggregates are very efficient quenchers even at very low concentrations, but under such conditions are difficult to be detected due to the low absorptivities. H-dimers absorb electromagnetic radiation at higher energies than isolated cations, and their bands overlap with a vibronic component of the electronic transition of the dye monomers. Hence, more probable interpretation of low emission from Ox4 is R6G self-quenching.

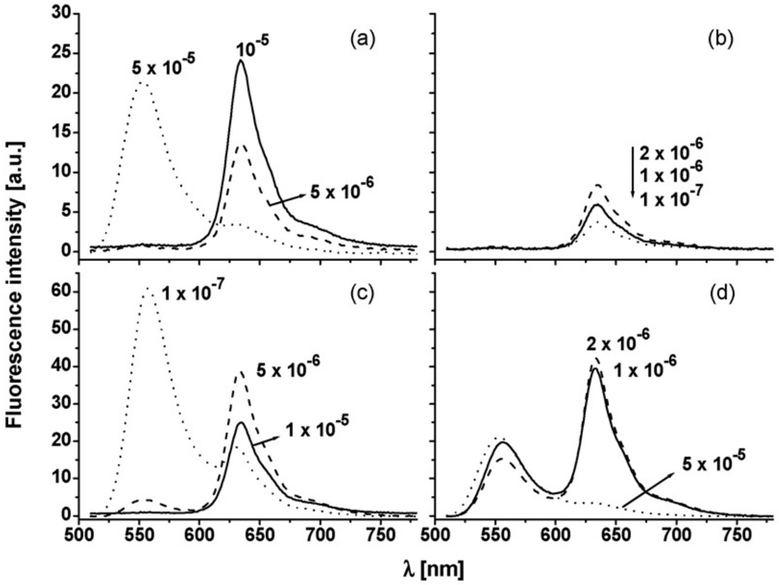

Fig. 3. Emission spectra of R6G/Ox4/Sum systems with varying concentrations of R6G (a and b) and Ox4 (c and d) after excitation at 500 nm. In (a and b) the concentration of Ox4 was constant (10^{-5} M), and the concentration of R6G varied from 5×10^{-5} to 10^{-7} M. In (c and d) the concentration of R6G was constant (10^{-5} M), and the concentration of Ox4 varied from 5×10^{-5} to 10^{-7} M.

The R6G concentration of 10^{-5} M was optimal for the energy transfer process. The band at 560 nm, assigned to the R6G emission, disappeared and only the band at 633 nm was detected in the spectrum. The disappearance of the donor band in favor of the acceptor emission is evidence for an efficient energy transfer. With the R6G concentration decreasing from 10^{-5} to 10^{-7} M, the intensity of the band at 633 nm attributed to the Ox4 emission gradually decreased. For the lowest concentration, the intensity was very low. This can be explained in terms of the relationship between the energy transfer efficiency and the amount of available energy donor molecules. Lowering the concentration of R6G might significantly reduce the number of R6G molecules, which were in the vicinity of the adsorbed Ox4 cations. Consequently, the yields of the energy transfer significantly decreased.

Similar experiments were performed for the reaction system, in which the concentrations of Ox4 were changed, and keeping the amount of R6G constant (Fig. 3c and d). The concentration of R6G was 10^{-5} M. The concentrations of the Ox4 solutions were 5×10^{-5}, 10^{-5}, 5×10^{-6}, 2×10^{-6}, 10^{-6} and 10^{-7} M. The optimal conditions for energy transfer were at the Ox4 concentration of 10^{-5} M. Under these conditions, the number of energy donor and acceptor molecules was equal. For the systems with the lower Ox4 concentrations (5×10^{-6}, 2×10^{-6}, 10^{-6} M), the intensity of the light emitted from the Ox4 monomers partially increased. This unexpected trend can be explained in terms of the fluorescence quenching due to the formation of the traces of Ox4 aggregates (which were not, however, detected) or more probably due to phenomenon of self-quenching, as a result of decreasing intermolecular distances at higher concentrations of fluorophores at interface. On the other hand, the decrease in the Ox4 concentration gradually increased the band for the emission from the R6G cations at 560 nm. This can be interpreted as a less efficient energy transfer due to lower concentration of the energy acceptor molecules. The overall decrease in both components lead to larger intermolecular distances, which consequently, lowers the efficiency of the energy transfer. For example, in case of the R6G and Ox4 concentrations of 10^{-5} and 10^{-7} M, respectively, which is the system of 100 R6G cations per one Ox4, the conditions for energy transfer were not sufficient. One can mainly see the emission from the R6G cations in this case. Only a low fraction of the energy was transferred and emitted from the Ox4 cations under these conditions (Fig. 3d). On the other hand, a relatively large energy was transferred in the system with the R6G and Ox4 concentrations of 10^{-5} and 10^{-6} M, respectively. Although there was only 1 Ox4 ion per 10 R6G cations, the emission from the former dye prevailed. In summary, the energy transfer in the smectite dispersions with R6G and Ox4 occurred most efficiently when equal and appropriately low (10^{-5} M) concentrations of the dyes are used. However, the efficiency of the process also remains relatively high in the cases when the concentration of Ox4 is partially reduced.

As mentioned above, the presence of some long-chain alkylammonium surfactants can decrease the formation of non-luminescent H-aggregates and thus increase the luminescence of laser dyes in dye/layered silicate films [35]. Coexistence of photochemically inactive alkylammonium ions may lead to the decrease of a local dye concentration at the interface, thus potentially reducing self-quenching. We tested the systems of R6G/Ox4 in a smectite dispersion, which included the surfactant, namely hexadecyltrimethylammonium cations. All of the components (dyes and surfactant) were of the same concentration (10^{-5} M). However, no significant changes were observed in the spectra and in the efficiency of the energy transfer process. The shape of the spectra and the intensities of the emission bands were almost identical to those for the systems without the surfactant. The extents of the dye aggregation can be efficiently controlled using suitable concentrations of the dye components.

4. Conclusions

The adsorption of laser dyes on the surface of smectite of low charge density was not accompanied with a substantial molecular aggregation. Dye monomers with optical properties similar to the forms present in dilute solutions were mainly detected using absorption and fluorescence spectroscopies.

The systems of smectite dispersions exhibited a fluorescence energy transfer, whereas it was absent in the solutions without the smectite under the same conditions. The smectite role was a suitable concentrating of the dye cations on its surface thus reducing their intermolecular distances.

Optimal conditions for the energy transfer were found at the medium concentrations of the dye components of 10^{-5} M.

Energy transfer from R6G to Ox4 and the emission from the Ox4 cations were substantially reduced when the concentrations of the dyes were higher. This phenomenon can be interpreted in terms of self-quenching, which proceeds via the energy transfer mechanism, but between excited and non-excited molecules of the same species. The formation of the dye molecular aggregates, which potentially could significantly contribute to the quenching of the luminescence, was not confirmed spectroscopically.

Lowering the concentrations of either the energy donor or acceptor led to a reduction in the energy transfer efficiency and/or emission from the Ox4 cations. Less cations on the smectite surface, which could be potentially active in FRET, leads to a lower concentration and larger intermolecular distances between the cations representing the energy donor and acceptor entities.

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