

Spectral Properties of Rhodamine 3B Adsorbed on the Surface of Montmorillonites with Variable Layer Charge

Juraj Bujdák,^{*,†} Virginia Martínez Martínez,[‡] Fernando López Arbeloa,[‡] and Nobuo Iyi[§]

*Institute of Inorganic Chemistry, Slovak Academy of Sciences, 845 36 Bratislava, Slovak Republic,
Department of Physical Chemistry, Faculty of Science and Technology, University of Basque Country,
Apartado 644. 48080- Bilbao, Spain, and National Institute for Materials Science, Namiki 1-1,
Tsukuba Ibaraki 305-0044, Japan*

Received August 17, 2006. In Final Form: November 2, 2006

Montmorillonite was thermally treated at several temperatures to reduce the charge density of its layer surface. Absorption and fluorescence (steady-state and time-resolved) spectroscopies are now applied to study the adsorption of rhodamine 3B (R3B) laser dye in reduced charge montmorillonites (RCMs) in aqueous suspensions. The decrease in the charge density increases the intermolecular distance between adsorbed R3B molecules, reducing the tendency of the dye to self-associate. H-type and J-type aggregates of R3B in RCMs are spectroscopically characterized, the fluorescent J-aggregates being more extensively formed by decreasing the charge density. Both the reduction in the dye aggregation and the formation of J-type aggregates enhance the fluorescence efficiency of R3B dye adsorbed in montmorillonite particles. Absorption with linearly polarized light reveals that the H-aggregates are more disposed toward the perpendicular of the clay surface than the monomer and J-aggregates species.

Introduction

Incorporation of photofunctional organic molecules into solid inorganic hosts can lead to the formation of novel hybrid materials. The design of new optical properties of hybrid materials based on organic dyes embedded in inorganic materials has been extensively investigated.¹ Rhodamine dyes are one of the most studied organic dye families. They are luminescent compounds frequently used in lasers, and their optical properties have been extensively analyzed.^{2,3,4} Rhodamines have been embedded in various inorganic materials such as clay minerals⁵ and other layered inorganics,^{6,7} silica⁸ and glasses,⁹ ceramics,¹⁰ sol–gel systems and other colloids,¹¹ porous materials,¹² etc.

There are numerous experimental works reporting the difficulties to achieve optimal luminescent properties of materials based on organic dyes incorporated in the solid host matrices. Not only selection of a suitable organic dye but also the choice

of an adequate inorganic host seems to be very important for the construction of hybrid optical materials.¹³ The relationship between surface parameters of inorganic templates and optical properties of adsorbed cationic dyes have been reported for various systems based on dye/clay mineral dispersions, e.g., dispersions with methylene blue.¹⁴ The adsorption of cationic dyes on a clay mineral surface is principally by electrostatic attraction, although van der Waals forces also contribute to the adsorption. The layer charge of clay minerals affects the formation of molecular assemblies of adsorbed dye cations. Similar trends were also observed for thin solid films based on intercalated cationic dyes in oriented thin films of expandable clay minerals.¹⁵ As an example, precise control of the interlayer arrangement was reported for rhodamine 6G (R6G) in the interlayer spaces of reduced charge montmorillonites (RCMs).¹⁶

Recently, the molecular aggregation of various rhodamine dyes on layered silicates was extensively investigated.¹⁷ The exciton theory describes the existence of fluorescent and nonfluorescent molecular assemblies as a function of their structures.¹⁸ The optical properties of rhodamine 3B (R3B) are relatively unchanged when adsorbed on the surface of layered silicates.¹³ Indeed, the absorption and fluorescence spectra of R3B adsorbed as monomeric units are very similar to those in aqueous solution but shifted to lower energies. Compared to other cationic rhodamines, R3B is a hydrophobic dye with diethyl groups at the N atoms of its molecular structure (Figure 1). Absorption and fluorescence spectra of R3B in smectite-type clays in aqueous suspension reveal that the presence of dialkyl groups in its molecule may prevent the formation of “sandwich-

* To whom correspondence should be addressed. E-mail: uachjuro@savba.sk. Tel.: +421-2-59410 459. Fax: +421-2-59410 444.

[†] Slovak Academy of Sciences.

[‡] University of Basque Country.

[§] National Institute for Materials Science.

(1) Ogawa, M.; Kuroda, K. *Chem. Rev.* **1995**, *95*, 399.

(2) López Arbeloa, F.; López Arbeloa, T.; Tapia Estévez, M. J.; López Arbeloa, I. *J. Phys. Chem.* **1991**, *95*, 2203.

(3) Kemnitz, K.; Yoshihara, K. *J. Phys. Chem.* **1991**, *95*, 6095.

(4) Beaumont, P. C.; Johnson, D. G.; Parsons, B. J. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 195.

(5) (a) López Arbeloa, F.; López Arbeloa, T.; López Arbeloa, I. *Trends Chem. Phys.* **1996**, *4*, 191. (b) López Arbeloa, F.; Tapia Estévez, M. J.; López Arbeloa, T.; López Arbeloa, I. *Langmuir* **1995**, *11*, 3211. (c) López Arbeloa, F.; Tapia Estévez, M. J.; López Arbeloa, T.; López Arbeloa, I. *Clay Miner.* **1997**, *32*, 97.

(6) Shinozaki, R.; Nakato, T. *Langmuir* **2004**, *20*, 7583. Ghanadzadeh, A.; Zanjanchi, M. A. *Spectrochim. Acta, Part A* **2001**, *57*, 1865.

(7) Bockstette, M.; Wohrle, D.; Braun, I.; Schulz-Ekloff, G. *Microporous Mesoporous Mater.* **1998**, *23*, 83.

(8) Kanezaki, E. *Mol. Cryst. Liq. Cryst.* **1996**, *275*, 225.

(9) (a) Kikteva, T.; Star, D.; Zhao, Z.; Baisley, T. L.; Leach, G. W. *J. Phys. Chem. B* **1999**, *103*, 1124. (b) Gruzdkov, Y. A.; Parmon, V. N. *J. Chem. Soc. Faraday Trans.* **1993**, *89*, 4017.

(10) Vogel, R.; Meredith, P.; Harvey, M. D.; Rubinsztajn-Dunlop, H. *Spectrochim. Acta, Part A* **2004**, *60*, 245.

(11) (a) del Monte, F.; Ferrer, M. L.; Levy, D. *Langmuir* **2001**, *17*, 4812. del Monte, F.; Mackenzie, J. D.; Levy, D. *Langmuir* **2000**, *16*, 7377. (b) Leng, X. J.; Starchev, K.; Buffle, J. *Langmuir* **2002**, *18*, 7602.

(12) Ferreira, L. F. V.; Lemos, M. J.; Reis, M. J.; do Rego, A. M. B. *Langmuir* **2000**, *16*, 5673.

(13) Bujdák, J.; Iyi, N. *J. Phys. Chem. B* **2006**, *110*, 2180.

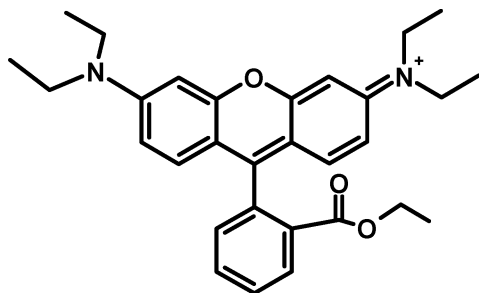
(14) (a) Bujdák, J.; Komadel, P. *J. Phys. Chem. B* **1997**, *101*, 9065. (b) Bujdák, J.; Janek, M.; Madejová, J.; Komadel, P. *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 3487.

(15) Bujdák, J.; Iyi, N.; Kaneko, Y.; Sasai, R. *Clay Miner.* **2003**, *38*, 561.

(16) Bujdák, J.; Iyi, N.; Kaneko, Y.; Czimerová, A.; Sasai, R. *Phys. Chem. Chem. Phys.* **2003**, *5*, 4680.

(17) Chaudhuri, R.; López Arbeloa, F.; López Arbeloa, I. *Langmuir* **2000**, *16*, 1285.

(18) Kobayashi, T. *J-aggregates*; World Scientific Pub Co.: Singapore, 1996.



Rhodamine 3B

Figure 1. Molecular structure of the rhodamine 3B cation.

type” H-aggregates (typically observed for the less hydrophobic R6G dye with monoethyl groups at the N atoms), but they favor the formation of “head-to-tail” J-type associations.^{19,20} The “head-to-tail” molecular assemblies, in contrast to the sandwich-type aggregates, exhibit luminescence and other interesting optical properties. Similar spectral profiles of R3B were observed for the dispersions with low- and high-charge layered silicates, represented by saponite and fluorohectorite, respectively.¹³ The presence of bulky hydrophobic groups in R3B cations probably causes large distances between interacting transition moments in aggregates, which makes exciton coupling less efficient and not significantly reflected in the optical properties. Besides the layer charge, swelling and colloid properties of inorganic template may significantly affect the dye molecular arrangement in the aggregates and, consequently, the optical properties of the dye adsorbed at the interface.

Larger resistance of R3B compared to R6G to form low-luminescent H-aggregates at interfaces makes this dye a good candidate to be an optical component for the design of new optical devices based on dye/inorganic host hybrid materials. Therefore, the objective of this work is a detailed spectroscopic investigation on the photophysics of R3B in a series of well-defined clay mineral specimens, represented by RCMs. RCMs were prepared from one parent material using Li^+ fixation (see Experimental Section for more detailed description). The composition, crystallinity, and other parameters were almost unchanged during the charge reduction. Therefore, the series of RCMs provides a unique model for probing the effect of the layer charge of clay mineral.²¹ This approach is more advantageous than testing the effect of the layer charge using the series of various samples of clay minerals characterized with variable charge but also different in many other parameters.

Experimental Section

Materials. RCMs were prepared from one parent Li^+ -montmorillonite Nanocor (N) using thermal treatment.¹⁶ Li^+ -saturated mineral had been prepared from the Na^+ -saturated form by an ion-exchange reaction with LiCl aqueous solution. Thermal treatment of N was performed at various temperatures (100, 110, 120, and 130 °C) for 24 h. The materials prepared by heating are denoted N100, N110, N120, and N130, where the number indicates the heating temperature used for the preparation of RCMs. The cation exchange capacity (CEC) of a Li^+ -saturated parent material, N, was 1.35 mmol/g. The samples with reduced charge exhibited partially lower CECs, which were 1.24 (N100), 1.18 (N110), 1.14 (N120), and 1.05 mmol/g (N130). The layer charge decrease was confirmed by other methods, and the clay mineral samples were characterized in detail elsewhere.¹⁶

(19) López Arbeloa, F.; Martínez Martínez, V.; López Arbeloa, T.; López Arbeloa, I. *Langmuir* **1998**, *14*, 4566.

(20) (a) López Arbeloa, F.; Martínez Martínez, V.; Bañuelos Prieto, J.; López Arbeloa, I. *Langmuir* **2002**, *18*, 2658. (b) López Arbeloa, F.; Chaudhuri, R.; López Arbeloa, T.; López Arbeloa, I. *J. Colloid Interface Sci.* **2002**, *246*, 281.

(21) Komadel, P.; Madejová, J.; Bujdák, J. *Clays Clay Miner.* **2005**, *53*, 313.

R3B (benzoic acid, 2-[6-(diethylamino)-3-(diethylimino)-3H-xanthen-9-yl]-ethyl ester, monohydrochloride) (Figure 1) of high purity (laser grade) was purchased from Lambda Physik and used without further purification. Due to lower solubility of the dye, R3B stock solution (5×10^{-5} M) was prepared in a 1:1 (v/v) water/ethanol mixture.

Methods. The visible spectra of the R3B/RCMs dispersions were measured on a Varian double-beam UV/vis spectrophotometer model CARY 4E. The concentration and loading of the dye in the dispersion were kept constant at 2.5×10^{-6} M and at 0.05 mmol/g, respectively, which were achieved by additions of a dye stock solution (5×10^{-5} M) to the clay mineral dispersions. The final concentration of clay mineral in dye/clay dispersions was $5 \times 10^{-3}\%$ (w/w). The spectra were measured at room temperature 1 min after mixing the dye solution with the silicate dispersion. Since the spectra of dye/silicate dispersions changed with time due to the processes of rearrangement and reorganization of the formed molecular aggregates, absorption spectra were also recorded after 2, 5, 10, and 20 min and 24 h aging times. The spectra of the clay dispersions without the dye, which mainly included light scattering from solid particles, were subtracted from the dye/silicate spectra. The evolution of the dye species with the aging time was checked by the time difference spectra (TDS) method, which was calculated by subtracting the absorbance values measured at different reaction times for each wavelength.

Fluorescence spectra were registered in the right-angle configuration on a Fluorolog 3-22 fluorimeter equipped with double monochromators in both the excitation beam and the detection channel and a red-sensitive photomultiplier. The measurements were performed at room temperature after excitation at 535 nm, and the backgrounds due to light scattering from clay mineral particles were subtracted by a similar procedure to that described for absorption spectroscopy.

Fluorescence decay curves were recorded by the time-resolved single photon counting technique in an Edinburgh Instruments SPC model FS920. The excitation was performed at 410 nm by means of a LDH-410 PicoQuant diode laser head working a 10 MHz of pulse repetition rate. The width of the excitation pulses was around 50 ps, providing a global time resolution of the instrument of 30 ps after deconvolution of the instrument response function (recorded by a LUDOX scattering dispersion). The recorded curves were analyzed by several exponential decays. The statistical significance of the fits was controlled by the chi-square (χ^2) and the Durbin–Watson (DW) statistical parameters.

The polarized UV/vis absorption spectra were recorded on Jasco spectrophotometer using a V-550 UV/vis spectrophotometer (Jasco Co., Ltd.) and a Jasco polarizer. A few drops of silicate suspensions were deposited on quartz slides by a spin-coating method in order to obtain thin films with a preferential orientation of silicate layered particles parallel to the slide surface. An ion-exchange reaction with dye cations was performed in ethanol/aqueous solution of volume ratio 1:1 and dye concentration 10^{-3} mol/dm³. The supported silicate films were immersed in the dye solution and heated at 60 °C for 2 h. Films with adsorbed dye were washed in deionized water and with ethanol in another step in order to remove the excess dye solution. A series of spectra was measured using both horizontally (x) and vertically (y) polarized light. The quartz slide with the dye/clay film sample was rotated around the x axis, changing the orientation of the slides with respect to the y axis only. More details on theoretical background and experimental setup of the method have been published elsewhere.²²

Results and Discussion

Absorption Spectroscopy. The effect of the layer charge of clay minerals has already been reported for the interactions of R6G with montmorillonite.²³ The layer charge favors the R6G aggregation, which generally is a sandwich H-type arrangement

(22) Chen, G. M.; Iyi, N. B.; Sasai, R.; Fujita, T.; Kitamura, K. *J. Mater. Res.* **2002**, *17*, 1035.

(23) Bujdák, J.; Iyi, N.; Sasai, R. *J. Phys. Chem. B* **2004**, *108*, 4470.

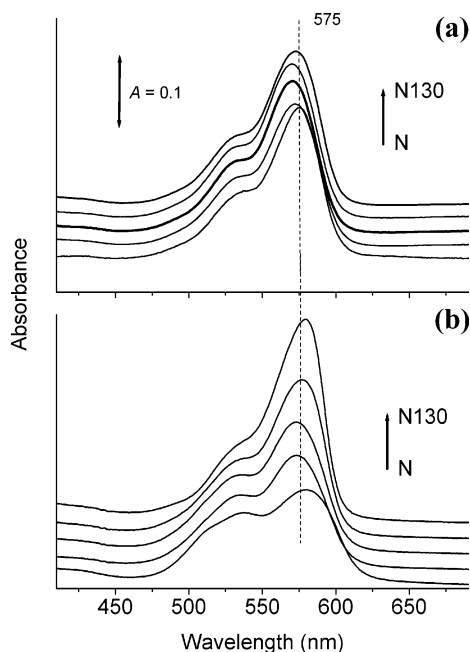


Figure 2. Absorption spectra of rhodamine 3B in montmorillonites dispersions. The spectra were recorded 1 min (a) and 24 h (b) after mixing the silicate dispersion with the dye solution.

for this dye. Moreover, the dye association increases with the aging time of the R6G/RCM dispersion, which is a general trend in rhodamine dyes, including R3B.¹³ This evolution, however, is opposite to the trend observed for methylene blue aggregation.¹⁴

Figure 2 shows absorption spectra of R3B in clay aqueous dispersions of RCMs. The dye loading of 0.05 mmol/g is much lower than the CEC of the materials (1.05–1.35 mmol/g). The spectra measured 1 min after mixing the dye solution with clay mineral dispersions are shown in Figure 2a. These spectra, characterized by a main absorption band centered at about 575 nm and a broad shoulder at around 530 nm, are very similar to each other and bathochromically shifted with respect to that recorded for diluted solution of the dye (560 nm).² The bathochromic shift was generally observed in the spectra for various dyes, including rhodamines,¹³ adsorbed at clay surfaces. The spectral shifts have been explained in terms of the effect of the polar environment of the clay mineral surface on dye electronic transition.²⁴ In other works, spectral shift was used as the parameter to estimate adsorption site of the dye cations. Lower bathochromic shifts have been assigned to the adsorption of the dye cations on the external surface of clay mineral particles with respect to internal surface.²⁵ A scheme showing various sites at clay mineral surface is shown in Figure 3. The present results suggest that the adsorption of R3B on RCMs surfaces took place just after mixing the dye and the silicates.

The main band slightly changed with the layer charge of clay mineral template (Figure 2a). These shifts could be attributed to either a modification in the micropolarity environment of the clay surfaces with the layer charge and/or the dye aggregations with H-band or J-band overlapping the monomer absorption band. Thus, the slight shift of the main absorption band at higher wavelengths of R3B in the N dispersion with respect to RCMs could be assigned to more polar environment for the non-thermal-treated N surface, due to its highest charge density (CEC = 1.35 mmol/g). On the other hand, the main absorption band of R3B

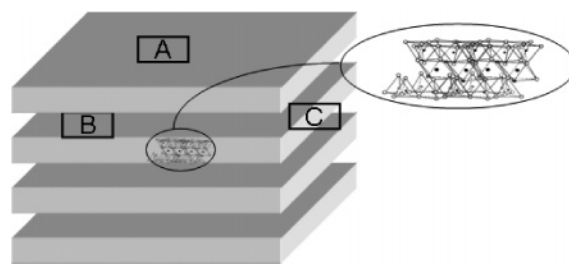


Figure 3. A schematic figure showing various sites at clay mineral surface, such as external (A), internal or interlayer (B), and particle edges (C).

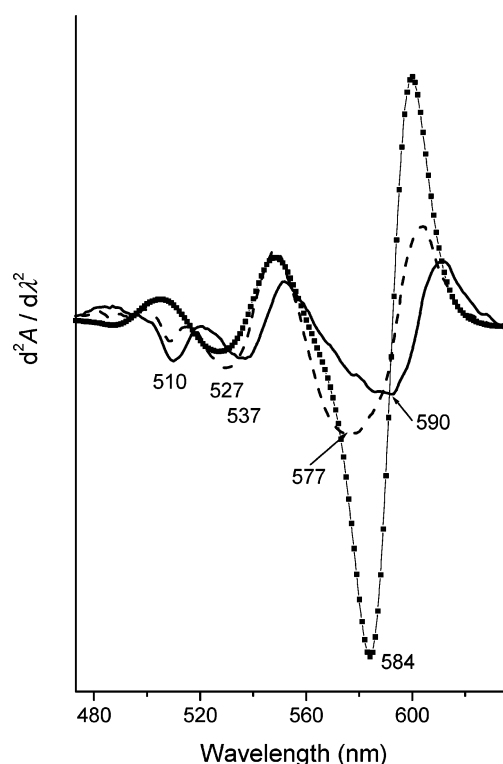


Figure 4. Second-derivative absorption spectra rhodamine 3B/montmorillonites of selected dispersions: solid line (N), dashed line (N110), and line + symbol (N130). Calculated from the spectra measured 24 h after mixing the silicate dispersion with the dye solution.

in moderate RCMs such as N100, N110, and N120 does not show an intermediate position between the highest (N) and the lowest (N130) layer charge silicate. Intercalation of the dye cations in N130 might be due to lower dispersion stability of this clay mineral sample²³ (formation of the tactoids in N130 dispersion can be further enhanced after the adsorption of the dye).

More important differences were observed for R3B spectra measured after 24 h, after the reorganization of dye cations on the surface have taken place (Figure 2b). With increasing layer charge, the absorbances of the bands placed at shorter wavelengths partially increase to the detriment of the absorption bands at longer wavelengths. This is clearly observed for the R3B/N dispersion, with a broader absorption band at 590 nm and two poorly resolved shoulders at the high-energy part of the spectrum. The shape and the positions of the absorption bands can be further investigated in detail using a second derivative spectroscopy (Figure 4). The bands with maximal absorptions at 536 and 510 nm are assigned to the H-band of dimers and large-size molecular aggregates, respectively. Dye aggregates with predominant H-absorption bands should be assigned to sandwich-type molecular arrangements. Sandwich H-type aggregates of R3B

(24) Neumann, M. G.; Schmitt, C. C.; Gessner, F. J. *Colloid Interface Sci.* **1996**, *177*, 495. Cenens, J.; Schoonheydt, R. A. *Clays Clay Miner.* **1988**, *36*, 214.

(25) Tapia Estévez, M. J.; López Arbeola, F.; López Arbeola, T.; López Arbeola, I. *Langmuir* **1993**, *9*, 3629.

have also been reported in other systems, such as in solutions,³ or at interfaces.⁷

H-bands of R3B aggregates are not so clearly observed for RCMs systems, for instance, the absence of the absorption band at 510 nm for the R3B/N130 system (Figure 4). The main band, which had been detected at 590 nm for the R3B/N dispersion, shifts to lower wavelengths with decreasing layer charge of clay mineral template. Also, the H-band of R3B dimer hypsochromically shifts by decreasing the charge density, from 537 (N) to 527 nm (N130). The red shift of the main absorption band of R3B/N with the aging could be suggested as the contribution of a J-band of a dye aggregate, as is mentioned above. Different positions of the main bands for R3B/N110 and R3B/N130 assigned to monomeric dye species can be explained in terms of the effect of a molecular environment around the chromophore units. Initially, R3B dye cations mostly occupy external surface in dilute clay mineral dispersions. However, face-to-face assemblies of montmorillonite particles (tactoids) are formed after partial neutralization of the surface charge after absorption of the dye cations. The surface charge neutralization is assumed to be most efficient especially in the case of the lowest charge silicate. Hence, the red-shift observed for the spectrum of R3B/N130 is probably related to the presence of the dye trapped at the sites of interlayer spaces of clay particle tactoids (Figure 3, site B). Fluorescent spectroscopy is a more suitable method than absorption spectroscopy for studying the effects of molecular environment on optical properties of dye cations. Therefore, the sites of dye adsorption are analyzed mainly in the interpretations on fluorescent spectra (see below).

Time-Difference Spectra. A comparison of the spectra measured 1 min and 24 h after mixing the clay dispersions with the dye solution does not provide detailed information on the relatively minor changes observed in the absorption spectra (Figure 2). A more precise evaluation of these changes can be derived from the TDS method, calculated by subtracting the spectrum of the aged system from that of a fresh one (Figure 5). Bands of positive absorption values represent species which decomposed with time, whereas negative difference bands are related to the formation of species with time. We do not assume decomposition of the dye cations in clay mineral dispersions, since this has never been reported, and TDS are considered to provide more detailed information on the dye aggregation/deaggregation with time.

In the present systems, the most extensive spectral changes are observed in R3B/N dispersion (Figure 5). The dye species formed with time (negative-difference absorption bands) are placed at shorter (around 505 nm) and longer (around 600 nm) wavelengths. The 505 nm band has been attributed to the H-band of high-order aggregates, and it is clearly identified in a second-derivative spectrum of this reaction system (Figure 4). The second negative difference band at 601 nm can be assigned to the J-band of a nonperfect sandwich aggregate and more probably to the formation of a head-to-tail molecular association.²⁶ This J-band cannot be distinguished either in the absorption spectra (Figure 2) or in the second-derivative spectra (Figure 4), probably due to the overlap with the broad absorption band of dye monomers, now clearly observed at about 575 nm by the positive TDS band. The low sensitivity of absorption spectroscopy to characterize the formation of R3B J-aggregates has been reported.³ The J-band of the head-to-tail aggregates formed for R3B solutions in nonpolar solvents overlapped with that of the monomers, due to a very low exciton splitting, and therefore, their existence was

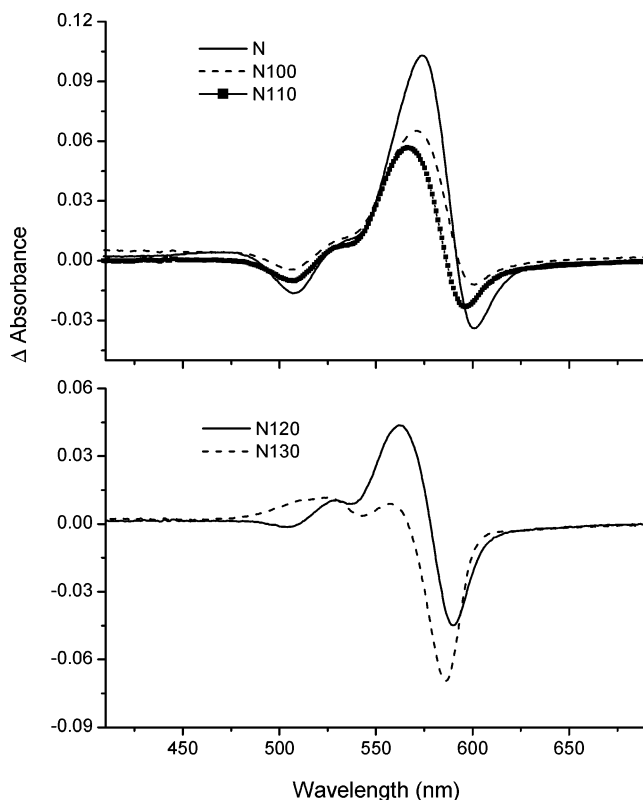


Figure 5. Time difference absorption spectra (24 h aged spectra minus the corresponding fresh-prepared ones) of rhodamine 3B in montmorillonite dispersions.

proved on basis of fluorescence kinetics.³ Indeed, formation of head-to-tail dimers and trimers of R3B has already been reported for the dispersions of other clay minerals.²⁰ The decrease in the absorbance at 575 nm TDS band (ascribed to R3B monomers) is much larger than the augmentation in the absorbance values for the negative difference absorption bands. These tendencies indicate a much higher absorptivity of the dye monomers than the dye aggregates (hypsochromic effect by dye aggregation).

The evolution of the TDS profile for R3B/N100 is similar to that of the R3B/N dispersion, although with a lower extent of dye aggregation (Figure 5). The position of the 507 nm absorption band (assigned to the H-band of high-order aggregates) is relatively constant, and the band at around 600 nm (J-band of aggregates) slightly shifts to higher energies (e.g., 596 and 601 nm for R3B/N100 and R3B/N, respectively). This may indicate some structural differences between aggregates formed at surfaces of respective clay minerals and/or a greater influence of the monomeric absorption band for the R3B/N100 system as a consequence of its lower tendency to dye aggregation. Further decrease in the layer charge (N120 and N130 silicates) is reflected in more substantial changes in the TDS trends (Figure 5). Formation of the H-aggregates is no longer observed (R3B/N130) or at least is not prominent (R3B/N120). The H-type sandwich aggregates (positive TDS bands at 500–530 nm) decompose with time, yielding dye monomers, absorbing at about 586 nm, as the only reaction product. Specific changes are observed for the R3B/N120 dispersion: the absorbing species at 562 nm converts to the products with TDS band at 590 nm. This reaction can be interpreted as the conversion of dye monomers to head-to-tail dimers. An alternative interpretation would be the change of the adsorption site of monomers from the external surface to the interlayer spaces of the clay mineral, as is discussed below.

(26) Chambers, R. W.; Kajiwar, T.; Kearns, D. R. *J. Phys. Chem.* **1974**, *78*, 380.

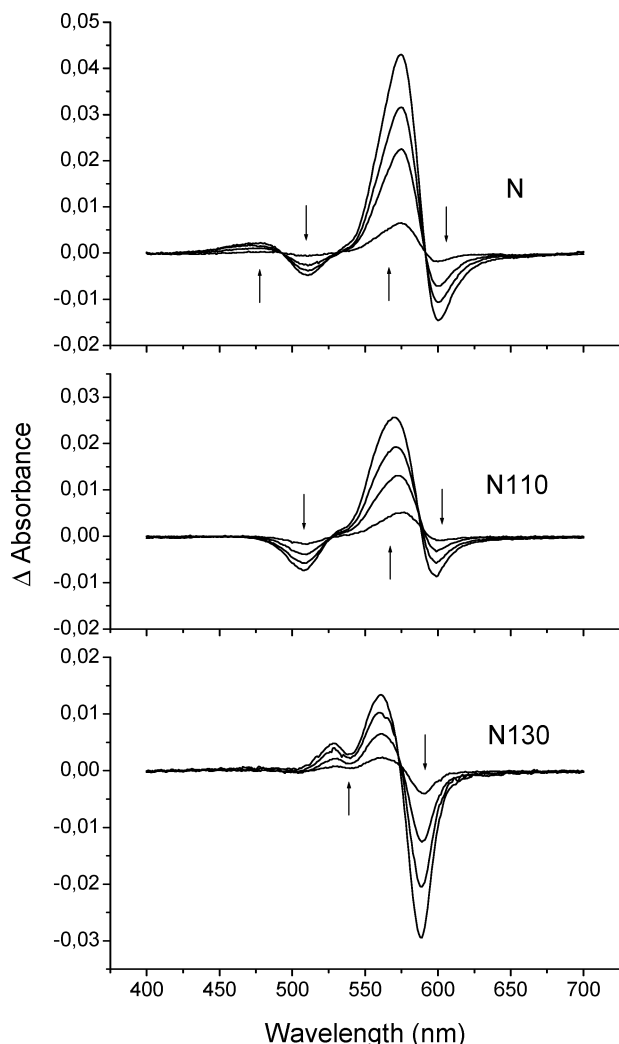


Figure 6. Representative time difference absorption spectra (aged spectra minus the corresponding 1 min aged ones) of rhodamine 3B/montmorillonites dispersions for initial stages of the reactions (2, 5, 10, and 20 min) for N, N110, and N130 silicates.

From these results, it is clear that the reorganization and redistribution of the dye assemblies with time are specific to the layer charge and/or to the swelling as charge-related property of clay mineral. It is generally known that the most significant changes in dye/clay mineral dispersions occur in the first minutes after their preparation, although a whole process of dye reorganization and rearrangement could take hours or days.^{14,24} Therefore, further series of spectra were measured in order to shed more light on the processes during initial stages of the reactions (1–20 min). Calculated TDS are shown in Figure 6. The TDS profile of R3B/N system indicates two adducts (at ~ 475 and 574 nm) and two reaction products (at 511 and 600 nm). The species, characterized with a broad absorption at about 475 nm, was not clearly observable in the TDS shown in Figure 5. This type of species of R3B may relate to the H-band of higher-order aggregates, which were initially formed at clay mineral colloid particles, probably at the most accessible zones of an electric double layer (at the external surface). This is very similar to the case of methylene blue, which has been reported elsewhere.²⁷ The amount of R3B species absorbing at 475 nm was relatively very low and decomposed in the first steps of adsorption. Its presence is detected only for R3B/N dispersions and was not found for other R3B/RCM systems. Identification

of other species, namely an adduct absorbing at 574 nm and reaction products characterized by the bands at 511 and 600 nm, is identical to the interpretations discussed above.

The shapes of TDS for R3B/N100 (not shown) and R3B/N110 are not much different from that of R3B/N. The extents of the reactions decrease with the layer charge reduction, as estimated from the amount of monomeric form (~ 570 nm), which converted to dye aggregates (both H- and J-bands). Interestingly, the H-band of dimers at 530 nm appears in TDS of N120 (not shown) and N130 dispersions as reaction product. Similar to the trends described in Figure 5, the reaction in N130 dispersion does not include formation of any H-band of aggregates (Figure 6, bottom). In this sample, only one reaction product characterized by absorption at 590 nm is formed and can be assigned to a specific form of the dye monomers trapped in clay mineral tactoids (at the interlayer space) or the J-band of a head-to-tail aggregate. The reactants in this case are sandwich dimers and isolated dye cations adsorbed at external surface. However, the decrease in monomers was mainly detected in the beginning of the reaction (Figure 6, bottom), whereby the amounts of the H- and J-type aggregates continually changed with time (Figure 5). The TDS evolution of R3B/N130 dispersion is similar to that previously observed for R3B in trioctahedral smectite, saponite SapCa-1.¹³ Also in the case of the R3B/SapCa-1 system, the conversion of the H-band of dimers and isolated ions to J-band of aggregates was reported. This fact could be related to similar layer charge of SapCa-1 and N130, as indicated by their CEC values, 0.95 and 1.05 mmol/g, respectively.

Fluorescence Spectroscopy. There are several aspects to be considered in the interpretation of fluorescence spectra for the systems containing dye molecular assemblies. First, aggregates of a perfect sandwich-type stacking are nonluminescent and twisted sandwich aggregates are generally nonfluorescent because of the very rapid internal conversion process from the highest H-excited-state to the lowest J-excited-state of these aggregates. The radiative transition probability from the J-excited-state to the ground state is very low, and sandwich-type aggregates act as efficient quenchers for the fluorescent emission of monomers and other coexisting fluorescent species. Second, the shape of emission spectrum from a single fluorophore component is independent of the excitation energy. Hence, spectral shape changes with the excitation wavelength would indicate the presence of more luminescent species coexistent in the system. However, the analysis of fluorescence spectra of multicomponent systems is complicated by the phenomenon of energy transfer processes between several excited states and species.

The emission spectra of R3B/N and R3B/RCMs systems were recorded after the excitation at 535 nm (Figure 7). This wavelength is close to that of the maximal absorption of H-type dimers (Figure 2) but also includes absorption by monomers, namely that related to a vibronic component of the electronic transition. Experimental results reveal that the R3B/N system exhibits unique luminescent properties. For the R3B/N system, the fluorescence emission involves a much broader range of wavelengths, mainly at short wavelengths (550 – 575 nm), which has not been observed for the other R3B/RCMs systems, with emission bands centered at around 590 nm (Figure 7). For this short-wavelength R3B emission band, together with the blue-shifted absorption bands (Figure 2), the R3B/N dispersion system is unique in its optical properties compared to R3B/RCMs dispersions. Therefore, one could consider the relationship between the features of its luminescent properties and the specific properties indicated in absorption spectra. Due to the presence of H- and J-type bands overlapping with the monomeric bands in the absorption spectra

(27) Bujdák, J.; Iyi, N.; Fujita, T. *Clay Miner.* **2002**, *37*, 121.

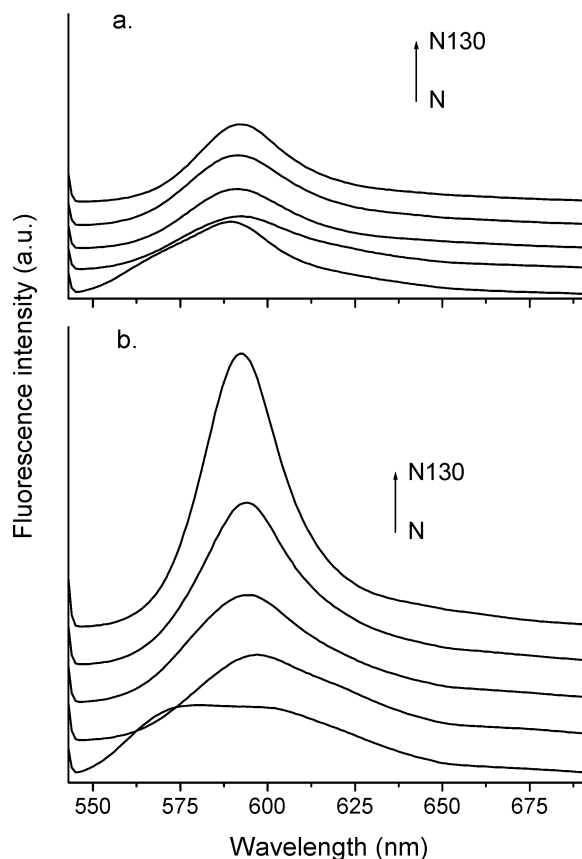


Figure 7. Emission spectra of rhodamine 3B/montmorillonites dispersions recorded after excitation at 535 nm. The spectra were measured 1 min (a) and 24 h (b) after mixing the silicate dispersion with the dye solution.

and the non- or poor-luminescence properties of sandwich-type aggregates, it was previously concluded that the dye aggregation in dye/clay dispersions can be studied in detail by absorption spectroscopy whereas fluorescence spectra provide a better characterization of monomer species.⁵

Absorption spectroscopy revealed formation of dye molecular assemblies in the R3B/N dispersion. Because of the high overlapping between the absorption bands of R3B monomers adsorbed at the external surface and the interlayer space of N tactoids and the J-bands of aggregates (all species absorbing in the 570–600 nm range), it is rather difficult to distinguish externally and internally adsorbed R3B monomers in N particles by absorption spectroscopy. Therefore, the fluorescent shoulder at lowest wavelengths observed for the R3B/N system (Figure 7) could be assigned to the emission from H-excited-state of the sandwich aggregates (dimer or high-order aggregates) or the fluorescence emission of R3B monomers adsorbed at different clay surface sites. The emission from the highest H-excited-state of aggregates should only be possible if the nonradiative internal conversion process to the associated lowest J-excited-state is much lower than the rate constant of the radiative deactivation from the H-excited-state or if the reversible nonradiative energy transfer from the lowest J-excited-state to the highest H-excited-state can compete with the radiative deactivation from these excited states to the ground state.²⁸ The first phenomenon could be discarded for the present R3B/N system since the excitation to other more clear H-bands of aggregates (for instance, at 500 nm) does not lead to a higher contribution of the fluorescence

band at 570 nm (spectra not shown). On the other hand, there is not any scientific reason to expect an important improvement in the reversibility of the nonradiative energy transfer to the excited-state of R3B H-aggregates in the R3B/N system, which is not observed in any R3B/RCM dispersions nor in other dyes/clays aqueous dispersion or solid films. Therefore, the most plausible explanation for the recorded fluorescent spectra of R3B/N system should be the emission from R3B monomers adsorbed at two different N surfaces.

In order to study in more detail the dynamics of the excited-state of R3B in N and in RCMs, the fluorescence decay curves of R3B/RCM dispersions were measured. Figure 8 shows some representative decay curves. Unfortunately, the exponential decay analysis of these curves is very complicated, and multiexponential analysis are required for the recorded decay curves according to eq 1

$$I_{\text{fl}} = \sum_i a_i \exp(-t/\tau_i) \quad (1)$$

where i is the number of exponentials and τ_i and a_i are the lifetime and the preexponential factor, respectively, for each component. Three-exponential analysis ($i = 3$) provides relative good fits of the experimental curves with χ^2 values in the 1.15–1.25 range. However, four-exponential decays ($i = 4$) improve the statistical parameter of the fits with χ^2 values in the 1.05–1.15 range. Table 1 lists the lifetime (τ_i) and contribution (a_i) of the decay curves analyzed as four-exponential decays, together with the corresponding amplitude average ($\langle \tau \rangle_{\text{aa}}$) and intensity average ($\langle \tau \rangle_{\text{ia}}$) values obtained by means of²⁹

$$\langle \tau \rangle_{\text{ia}} = \frac{\sum a_i \tau_i^2}{\sum a_i \tau_i} \quad (2)$$

$$\langle \tau \rangle_{\text{aa}} = \sum a_i \tau_i \quad (3)$$

These multiexponential decays reveal the presence of several ambiances for a unique fluorescence species and/or the fluorescence of several species and/or complex dynamic processes (including energy-transfer processes) involving several excited states. Due to the difficulties to give a physical interpretation for four-exponential decays, probably with overlapping fluorescence species, it is not possible to assign each lifetime. In preceding papers of R6G in Laponite films,³⁰ it was concluded that emissions from J-excited-states of R6G aggregates have longer lifetimes than the corresponding monomeric units. One of the decay components for R3B/RCM dispersions has a very short lifetime of 50 ps with preexponential factor of 30–40% of total contributions for freshly prepared dispersions (Table 1). Taking into account that a dilute R3B aqueous solution has a lifetime of 1.53 ns,² present results suggest an efficient quenching process for the fluorescence emission of R3B monomers, for instance, the energy transfer to the low-lying J-excited-state of aggregates. This behavior is common in all R3B/N and R3B/RCM systems and discards the possible emission from the highest H-excited-state of sandwich aggregates as being responsible for the detected emission at 570 nm for the specific R3B/N system.

As is mentioned above, the adsorption of dyes in clay surfaces generally shifts the absorption and emission bands at longer wavelengths due to changes in the environmental polarity. Because these changes should be more important in the interlayer

(28) Bojarski, P.; Matczuk, A.; Bojarski, C.; Kawski, A.; Kukliński, B.; Zurkowska, G. Dile, H. *Chem. Phys.* **1996**, *210*, 485.

(29) Valeur, B. *Molecular Fluorescence. Principles and Applications*; Wiley-VCH: Weinheim, 2002.

(30) Martínez Martínez, V.; López Arbeloa, F.; Bañuelos Prieto, J.; López Arbeloa, I. *J. Phys. Chem. B* **2005**, *109*, 7443.

Table 1. Fluorescence Lifetime (τ_i , in ps) and Contribution (a_i , %) for the Recorded Fluorescence Decay Curves Analyzed as Four-Exponential Decays after Deconvolution of the Instrumental Response Function of R3B/N and R3B/RCM Dispersions after 1 min and 24 h of Sample Preparation^a

	N		N100		N110		N120		N130	
	1 min	24 h	1 min	24 h	1 min	24 h	1 min	24 h	1 min	24 h
τ_i (a_i)	40(28)	50(13)	40(33)	60(23)	55(32)	60(24)	65(40)	55(24)	60(34)	60(38)
	240(32)	290(16)	230(19)	320(23)	260(24)	300(25)	280(28)	280(28)	220(29)	250(36)
	930(15)	1320(47)	860(25)	1160(31)	900(25)	1050(31)	900(21)	910(30)	660(25)	830(28)
	1880(26)	2520(24)	2360(23)	2800(23)	2400(18)	2720(20)	2280(11)	2480(18)	1900(12)	2290(6)
χ^2	1.15	1.09	1.09	1.11	1.13	1.06	1.12	1.11	1.16	1.09
$\langle\tau\rangle_{aa}$	710	1300	810	1090	750	960	550	810	460	420
$\langle\tau\rangle_{ia}$	1490	1840	1810	2050	1700	1920	1400	1700	1050	1150

^a The chi-square (χ^2) of the fittings and the amplitude average ($\langle\tau\rangle_{aa}$) and intensity average ($\langle\tau\rangle_{ia}$) lifetimes are also included.

space than at the clay/water interface (external surface), the absorption and fluorescence monomeric bands with the highest bathochromic shifts should be ascribed to dye molecules adsorbed into the interlayer space of clay tactoids. On the basis of these arguments, the fluorescent band at 590 of R3B/N dispersion should be assigned to R3B monomers intercalated in the interlayer space of N tactoids and the 570 nm emission band should be attributed to externally adsorbed R3B monomers. The absorption bands of these R3B monomers cannot be experimentally distinguished because of the overlapping with other J-bands of dye molecular assemblies (both sandwich and head-to-tail aggregates). The emission spectra of R3B/RCM dispersions are characterized by a dominant fluorescent band centered at about 590 nm, which should be ascribed to the emission from R3B monomers adsorbed in the interlayer space of RCMs, in accordance with the above interpretation.

R3B molecules adsorbed at the external surface of N tactoids could be present as monomeric units, characterized by the fluorescent band at 570 nm, and even as aggregates, characterized, for instance, by the positive difference TDS band exclusively observed for the R3B/N dispersion at around 470 nm (Figure 6, top). The non-observation of R3B species adsorbed in the external surface of RCM silicates (absence of the 570 nm emission band and the TDS band at 470 nm) should be related with the charge density of the clay layers. Highly charged layers (i.e., N dispersions) would induce more compact tactoids with a less accessible interlayer space, and the dye molecules would be adsorbed at the first steps in the more accessible external surface. By decreasing the charge density, the interlayer space becomes more accessible and internally adsorbed species are observed immediately after mixing dye and clay suspensions. This should be the case for R3B/RCM systems.

In order to analyze the time-evolution of the 570 nm fluorescence band, the emission spectra of R3B/N dispersion have been recorded for short aging times after sample preparation (Figure 9). The experimental results suggest that the externally adsorbed monomer with emission band at 570 nm does not exhibit any important time evolution, discarding any important change from externally to internally adsorbed species mentioned above. However, the 590 nm emission band, ascribed to internally adsorbed monomers (in interlayer spaces), is transformed to other emission bands placed at longer wavelengths. The deconvolution of the experimental fluorescence spectrum of the R3B/N system after 24 h of aging (taken from Figure 7b) in three Gaussians provides emission maxima at 570 (externally adsorbed monomers, Figure 3, site A), 595 (internally adsorbed monomers, Figure 3, site B), and 626 nm (J-band of R3B aggregates).

In contrast to R3B/N dispersion, an aging time of 24 h does not provide new emission bands for R3B/RCM systems (Figure 7) but rather enhances the emission intensity of the internally adsorbed R3B monomers. This enhancement with time progres-

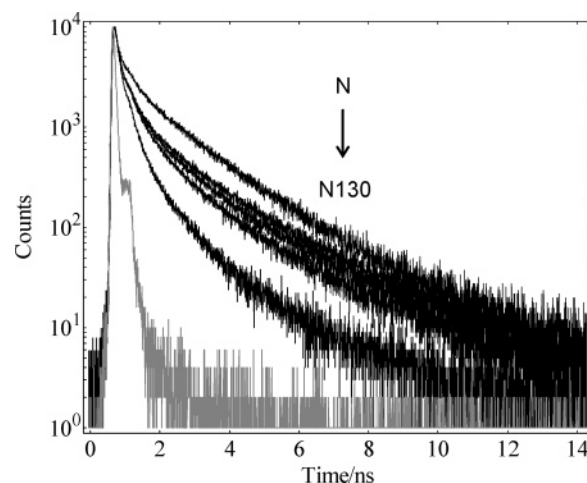


Figure 8. Fluorescence decay curves recorded at 595 nm after excitation at 410 nm of rhodamine 3B/montmorillonites dispersions. The recorded instrumental response signal is also shown (gray curve).

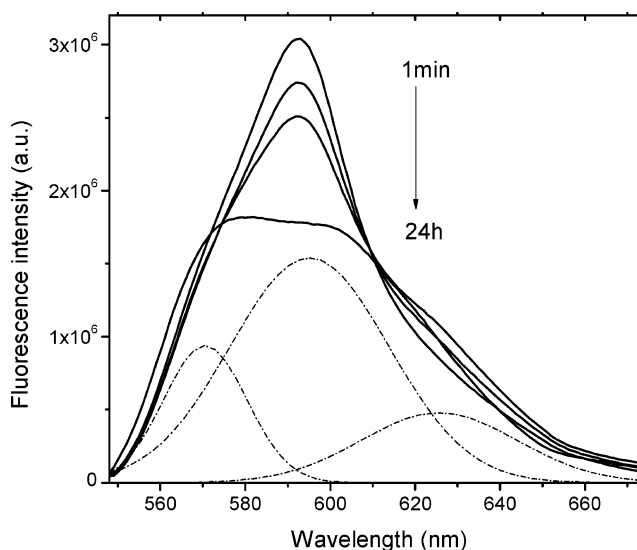


Figure 9. Time evolution of the fluorescence spectrum rhodamine 3B/N system with the aging time. Spectra were recorded after 1, 6, and 20 min and 24 h after mixing the silicate dispersion with the dye solution. The spectrum recorded after 24 h is deconvoluted in three Gaussian-type curves (dashed lines).

sively increases with decreasing layer charge of the silicate, being maximal for N130 and minimal for N100. These results could suggest a slight disaggregation process with the aging time of the internally adsorbed R3B species, increasing the emission from monomers by two phenomena: the higher proportion of monomers and the reduction of the fluorescent quenching by the aggregates. Such a disaggregation phenomenon could be related

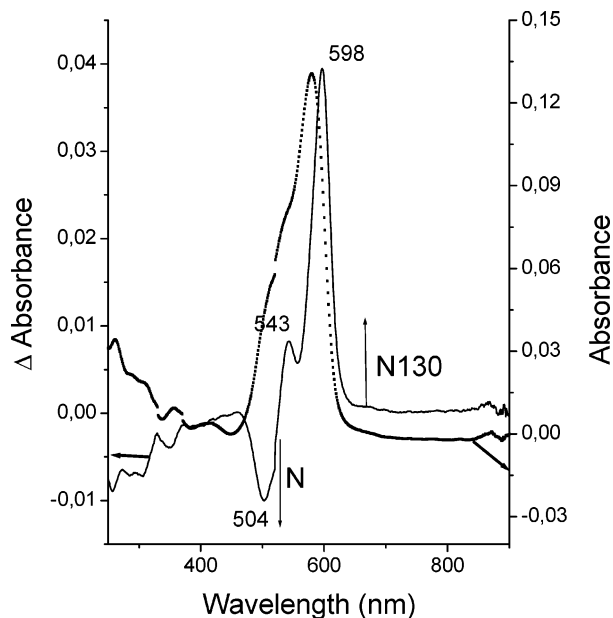


Figure 10. Absorption spectrum of rhodamine 3B/N film recorded using Y-polarized light at film tilt of 40° between the vector of light propagation and a surface normal (scatter). The spectrum is compared with difference absorption spectrum between the films of rhodamine 3B/N and rhodamine 3B/N130 (line).

to a more homogeneous and extended redistribution of the R3B molecules adsorbed in the interlayer space with the aging time.

Experimental data from fluorescence decay curves (Table 1) could confirm these interpretations. Previous results for R6G/laponite solid films suggested that the fluorescence lifetimes of R6G aggregates are higher than that of the R6G monomer.³⁰ Consequently, the aggregation of the R3B/N dispersion with the aging time can be analyzed by either the augmentation of the longest lifetime component (from 1.88 to 2.52 ns) and the diminution in the contribution of the shortest lifetime component (from 28% to 13%) by increasing the mixing time from 1 min to 24 h for the R3B/N dispersion. Besides, the shortest lifetime (that is ascribed to quenched R3B monomers) has the least contribution for the 24 h aged R3B/N dispersion. On the other hand, the lower tendency of dye association for the R3B/N130 system and the disaggregation process with the aging time could be related, respectively, to major contribution (>35%) of the shortest lifetime (around 60 ps) component and to the diminution of the contribution (from 12% to only 6%) of the longest lifetime (around 2 ns) component.

Dye/Clay Mineral Thin Films. Y-polarized spectra were measured at film tilt of 40° to enhance absorption of the molecules with a perpendicular orientation.²² The absorption spectra of the films were similar and not affected significantly by the layer charge of clay mineral templates. An example of the spectrum for R3B/N film is shown in Figure 10. The spectrum is dominated with a band at about 580 nm, which is assigned to the dye monomers possibly overlapped with the absorption assigned to J-type molecular assemblies. Besides the main band, only a shoulder at higher energies was clearly identified and assigned to a vibronic component, which could include transitions of potentially present H-dimers and larger-size H-aggregates. Difference absorption spectra were calculated to see, in more detail, if there is a systematic difference between the dye species compositions in the films. The R3B/N film exhibited a few more H-aggregates than those containing RCMs. Figure 10 (line) shows a representative difference spectrum calculated by subtraction of the spectrum of a R3B/N film from that of a R3B/N130 one.

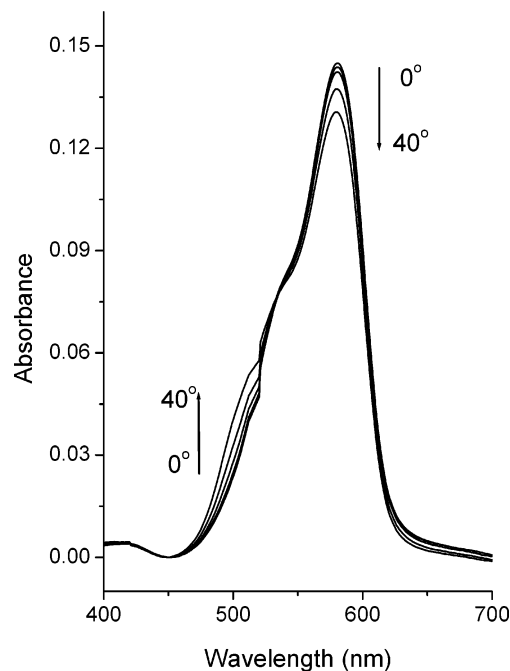


Figure 11. Absorption spectra of rhodamine 3B/N film tilted round X-axis at the angles 0°, 10°, 20°, 30°, and 40° measured using Y-polarized light. The arrows show evolution of the spectra with the change of film tilt angles.

The difference spectrum indicates slightly higher amounts of H-aggregates (504 nm) in the N film at the expense of dye monomers (543 nm) and J-dimers (598 nm). Other difference spectra exhibited similar trends with relatively fewer molecular aggregates in the films composed from RCMs (not shown). This trend was very similar to that observed for the dispersion systems (Figure 2).

Figure 11 shows an evolution of the spectra of R3B/N film with the twisting angle from 0° to 40°, recorded using Y-polarized light. H-aggregates of rhodamine dyes are known to be characterized with a nearly perpendicular molecular orientation at layered silicate surfaces and thus can be more sensitively detected when increasing the angle between the surface normal and a vector of light propagation.²² Slightly enhanced light absorptions at high energies (at around 500 nm) was observed in Y-polarized spectra at larger twisting angles (Figure 11) but absent in X-polarized ones (not shown). This proves the presence of nearly perpendicularly oriented R3B cations, assigned to H-aggregates, although in relatively low amounts.

Both the X- and Y-polarized spectra were measured at various film tilt angles to quantify the molecular orientation of the chromophores for all oriented films of R3B/RCMs. Figure 12 (scatter) shows the calculated angle distribution for the dye species in R3B/N film characterized with the wavelength of absorbed light. The angle determined for the species absorbing nearby 500 nm was around 45°. As mentioned above, this form can be assigned to the H-aggregates of R3B.³¹ The slightly tilted orientation was determined for the dye dimers and isolated dye cations being in the range 25–30° (Figure 12, scatter). These findings are in accordance with those observed for the films of fluorohectorite and saponite, which were saturated with the same dye.³¹ Similar to the trends of absorption spectra, the analysis of the dye molecular orientation revealed only a negligible effect of a clay mineral template. We calculated the difference values between orientation angles obtained for different films, which

(31) Bujdák, J.; Iyi, N. *J. Phys. Chem. B* **2005**, *109*, 4608.

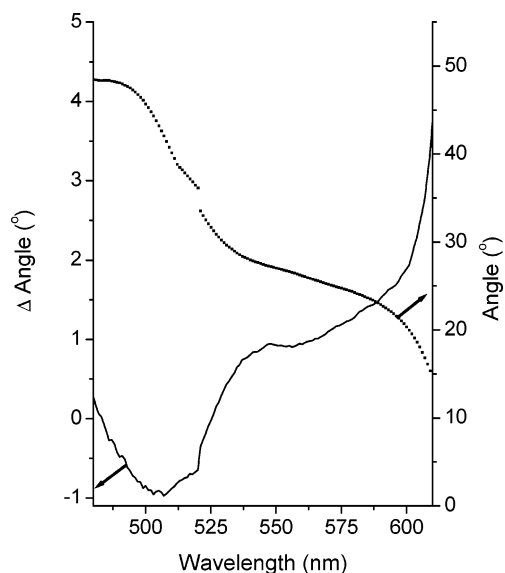


Figure 12. Molecular orientation angles determined for rhodamine 3B/N film (scatter) as a function of wavelength. Orientation angles are compared with difference values between molecular orientation of rhodamine 3B in N and N130 samples (solid line).

approached the experimental error of the method being in range -1° to $+2^\circ$ (Figure 12, line)

In summary, the clay mineral template slightly affects molecular aggregation of R3B in the films, which is interpreted in terms of the influence of the layer charge of silicate host on the distribution of dye cations at the mineral surface. This influence applies for different reaction systems, such as colloids and thin solid films, which is an interesting feature of R3B dye/clay mineral interaction.

Conclusions

The fluorescent emission of R3B dye adsorbed on clay mineral particles dispersed in water can be improved by reducing the charge density of the clay surface. Indeed, the diminution of the charge density, at least to some extent, by thermal treatment of montmorillonite clay reduces the dye aggregation, mainly the

formation of H-type sandwich aggregates which are efficient quenchers for the fluorescent emission from monomers. Lower charge density at the clay surfaces would increase the intermolecular distance between adsorbed R3B molecules, reducing the self-association tendency of the dye. For low-charge clay minerals, fluorescent J-type aggregates are favored and the aging of the sample induces the deaggregation of the dye, improving its fluorescence ability. The H-aggregates are adsorbed with relatively larger molecular orientation angles with respect to the plane of clay mineral surface than monomers and J-type aggregates.

This work proves that the trend of R3B molecular aggregation with the layer charge of clay mineral template is similar to other rhodamine dyes, although the variation of the optical properties is much lower. Choosing an appropriate clay mineral template can further improve the resulting optical properties of adsorbed R3B. The application of the hybrid materials based on layered hosts offers new perspectives, which cannot be provided by similar amorphous materials, since the former enables an oriented arrangement of dye molecules. This property opens new possibilities for materials chemistry on a molecular basis. The knowledge of this work is applied in further development of perspective optical materials. We continue in the research of an anisotropic transfer of electromagnetic energy based on the oriented arrangement of chromophore dipoles embedded in layered materials. On the basis of the results of this study, R3B was chosen as one of the dye components in the energy-transfer process. This dye exhibits optimal properties in an adsorbed state in combination with layered silicates characterized with low charge density.

Acknowledgment. This work was supported by the Slovak Research and Development Agency under Contract No. APVV-51-027405. We thank the Integrated Centre for Advanced Materials and Molecular Science IIC-MATMOL (Centre of Excellence supported by EU project G5MA-CT-2002-04051) for financial support of a research stay of Juraj Bujdák at University of the Basque Country.

LA062437B