Study of the Resonance Energy Transfer Between Two Dye Cations Embedded in Layered Silicates

A. Czimerova[1,*], J. Bujdák[1,2,†]

[1] *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia*
[2] *Comenius University in Bratislava, Faculty of Natural Sciences, Bratislava 4, Slovakia*

The Langmuir – Blodgett (LB) method is one of the useful techniques to prepare ultra-thin films with precise organization of embedded dye cations. The main limitations for the preparation of LB films is that the surfactants, building blocks of the LB films, must be amphiphiles and not soluble in water. In our study we used laser dye cation (rhodamine) with long alkyl chain in the structure, which makes this cation sufficiently hydrophobic. The alkylammonium chain helps to prevent dye molecular aggregation. The objective of this study was to prepare LB films built from synthetic saponite particles and adsorbed alkylammonium and organic dye cations. Energy transfer between two dye cations in LB films was studied. Oxazine 4 – energy acceptor molecules - does not represent an amphiphilic molecule, and is soluble in water. This problem we solved using long chain alkylammonium solution as the third component. We found out RET proceeded with high yields. The molecules of rhodamine played the role of molecular antennas absorbing green light (energy donor). Resonance energy transfer was detected as a quenching of light emission from rhodamine (~580 nm) in favour of the red light luminescence from oxazine (~ 623 nm), playing the role of energy acceptor.

1. INTRODUCTION

Incorporation of organic species into inorganic matrix has received significant attention from scientific and practical points of view [1]. From the practical point of view this type of inorganic-organic nanocomposites are potentially applicable in various fields, such as tunable lasers, memory storage media, but also in biomedical applications such as chemical sensors [2, 3]. From the scientific point of view, such hybrid systems often exhibit superior physico-chemical properties, which are frequently substantially different from the properties of components, the hybrids are built from [4].

The process of resonance energy transfer (RET) is a physical phenomenon which is important in chemical, physical and biomedical research [5]. The process may occur between two different molecules of fluorescence dyes which are in close proximity. The first molecule, called energy donor (ED), initially absorbs a quantum of electromagnetic radiation and becomes excited. If there is no second molecule, which could play the role of energy acceptor (EA) in the vicinity of EA, the molecule would relax back to the grand state via radiative or non-radiative deactivation processes [6]. If there is EA molecule in the vicinity of EA, energy transfer takes place. After the transfer of the energy, the acceptor molecules become excited; which can yield to an EA photon emission. In practice, the energy transfer leads to the reduction of fluorescence emission from ED molecules and to the increase of the fluorescence from EA molecules. There are many factors which influence the process and efficiency of RET. Absorption spectrum of EA must overlap with the emission spectrum of ED. There must be a short distance between interacting dye molecules to get a significant yields of RET. The parameter characterizing relative efficiency of a pair of dye molecules for RET is called as a Förster distance. It expresses the distance for 50% RET efficiency and is typically between 10 – 100 Å [6].

One of the most promising groups of inorganic matrices are layered silicates, mainly smectites. Due to the isomorphic substitutions, their layers bear a negative charge, which is balanced by hydrated inorganic cations. The cations can be easily exchanged by organic ones. Moreover, the negative charge and the layered structure are responsible for macroscopic swelling and other important physico-chemical properties [7].

The adsorption of dye cations on a smectite surface is a very complex reaction [8]. The first step represents an ion-exchange. It is a very fast almost instantaneous process [9]. At this step the exchangeable, mainly inorganic cations are exchanged by organic dye cations. After this step the reorganization and aggregation of the dye cations occurs, which may take several hours. In general, there are two types of molecular aggregates, H-, and J-aggregates. The H-aggregates are face-to-face intermolecular assemblies. Dipole alignment in H-aggregates induces the electrostatic repulsion, which causes an increase of the excitation energy compared to that of dye monomers [10]. Besides these species, J-aggregates can form. They are luminescent specie with a head-to-tail molecular association of dye cations.

* Adriana.Czimerova@savba.sk
† Juraj.Bujdak@savba.sk

Dipole attraction in J-type assemblies leads to the decrease of excitation energy, and the shift of spectral absorption band to higher wavelengths [11]. These two types of aggregates have different spectral properties. The J-aggregates may exhibit high fluorescence. The H-aggregates are mostly non-fluorescent even in the cases if they are built from fluorescent monomers. Moreover, They may significantly quench the fluorescence of other coexisting species. In general, the formation of H-aggregates is a crucial problem in the preparation of highly fluorescent materials on layered silicate templates. Sasai et al. [12] reported R6G molecular aggregation could be efficiently minimized and luminescence of the adsorbed dye molecules be increased in the presence of long-chain cationic surfactants [13].

In our previous studies we have reported RET between rhodamine 6G and oxazine 4 in synthetic saponite dispersions and thin films [14, 15]. The thin films were prepared using a spin-coating method. It was found that the presence of smectite in colloid induced RET, whereas thisphenomenon was absent in mixed dyes solution under the same conditions and in absence of smectite colloidal particles. However, fluorescence of both rhodamine 6G and oxazine 4 was substiantialy reduced when the concentrations of the dyes were too high. This phenomenon was interpreted in terms of a self-quenching, which proceeds via RET mechanism between excited and non-excited molecules of the same species and ending in non-luminescent H-aggregates, representing EA of the process. In case of spin-coated films, the quenching was more problematic [15]. The problem was solved by an appropriate modification of the inorganic material with hydrophobic alkylammonium cations. After this modification, the energy transfer was clearly proven. In addition, the series of reduced charge montmorillonite were prepared and the effect of charge reduction on the energy transfer process was studied [16]. Optical properties of rhodamine 3B and oxazine 4 in dispersion of reduced charge montmorillonite were significantly influenced by layer charge and other properties of montmorillonite template; mainly swelling properties. Similarly to fluorescence of individual dyes, the energy transfer proceeded in relatively highest yield at the samples with medium charge density. High-charge montmorillonites induced the formation of molecular aggregates which quenched luminescence from rhodamine cations. The lowest-charge montmorillonite induced large intermolecular distances between adsorbed dye cations, which reduced the energy transfer yields [16].

The main objective of this work was to prepare the Langmuir-Blodgett films (LB) based on smectite particles with adsorbed cations of two dyes, rhodamine B octadecylester perchlorate and Oxazine 4. The dyes were selected so that the phenomenon of RET can be achieved. We tried to found optimal conditions for achieving RET of high yields.

2. MATERIALS

The synthetic saponite Sumecton SA (Sum) was purchased from Kunimine Industries, Co., Japan. The cation exchange capacity of SUM sample was 0.87 ± 0.05 mmol.g^{-1}[17].

Octadecyltrimethylammonium bromide (ODTMA) was purchased from Sigma Aldrich and used as received. The laser dyes Rhodamine B octadecylester perchlorate (Sigma Aldrich) (RhBO) and Oxazine 4 (Ox4) were purchased from Lambda Physik GmbH (Göttingen, Germany) and used without further purification. The structure of the dyes is shown in Fig. 1.
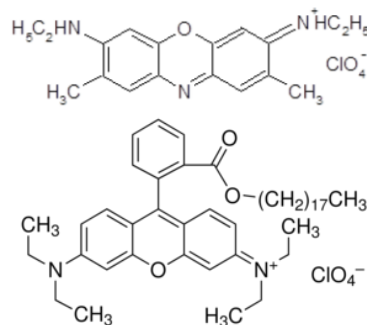

Fig. 1 – The molecular structure of used cationic dyes: Oxazine 4 (upper) and Rhodamine B octadecyl ester perchlorate (lower)

3. EXPERIMENTAL

3.1 Preparation of Langmuir-Blodgett films of clay / alkylammonium/dye systems

LB films were prepared on a Nima technology model 611 LB trough at a temperature 23°C. A milli-Q water and dilute saponite suspension with concentration 50 mg·dm^{-3} were used as a subphase. The solution of ODTMA with concentration 1×10^{-3} mol·dm^{-3} was prepared in ethanol. The solutions of RhBO and Ox4 with concentration 1×10^{-3} mol·dm^{-3} were prepared in a mixture of chloroform a methanol (9:1). The mixture of Ox4 with ODTMA was prepared in volume ration 1:1.The mixture of three components (ODTMA, RhBO, OX4) was prepared in ratio: 50:1:50% CEC. The cations in this mixture played the role of a surfactant in the preparation of LB films. A microsyringe was used to spread 40 μl surfactant solution over the subphases. After 30 minutes the film was compressed at a rate of 30 cm^2·min^{-1}. A floating film was transferred by horizontal dipping onto a hydrophobic glass plate at a surface pressure of 15 mN·m^{-1}. Before the deposition, glass slides were thoroughly cleaned by immersion into chromic acid and washed with de-ionized water.

3.2 Absorption and Fluorescence Spectroscopy

The absorption spectra of prepared LB films were measured in the visible range of electromagnetic radiation using Cary – 100 (Varian Inc.) spectrophotometer. The emission spectra of individual and two dye component LB films on Sum sub-phase were registered on Fluorolog-32 Horiba Jobin Yvon spectrofluoromether. The excitation at 500 nm was performed in all cases.

4. RESULTS AND DISCUSSION

The method for the preparation of LB films is one of the useful techniques to prepare ultra-thin and very precise organization of films [18]. In this case a stable molecular monolayer is transferred from the air-water interface to a solid substrate. When a solution of organic molecules is spread over a clay subphase, the solvent evaporates immediately and organic molecules during an ion-exchange reaction with clay formed densely packed monolayers at the air-water interface [19]. The main limitations for preparation a sufficient LB film is that the surfactants must be amphiphiles and not soluble in water [20]. Oxazine 4 – used as EA - does not represent an amphiphilic molecule, and is easily dissolved in water. This problem we solved using long chain alkylammonium solution (ODTMA).

Fig. 2 shows the surface pressure – area per molecule $(\pi - A)$ isotherms of the monolayer of RhBO/Ox4/ODTMA prepared in a saponite sub-phase. Surface pressure isotherm on saponite sub-phase rises gradually up to 42 mN·m^{-1}. At this point, the floating monolayer is collapsed. The isotherm in presence of saponite showed distinct phases before the collapse was reached. In comparison with a water sub-phase (not shown) no phases were detected. The specific behaviour of the Sum colloid is because of the electrostatic interactions between cationic dyes and saponite occurring at an air-water interface. Thus the saponite particles are concentrated at the air-water subphase and incorporated into LB monolayer [20].
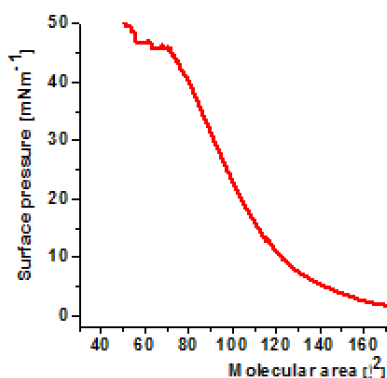

Fig. 2 – Surface pressure versus molecular area isotherms of monolayers of the mixture RhBO/Ox4/ODTMA prepared for SUM colloid (the ratio of RhBO/Ox4/ODTMA was 1 : 50 : 50% of CEC of SUM)

The absorption spectra of LB films of individual RhBO molecules and OX4/ODTMA at the Sum sub-phase were very similar (not shown). In the case of RhBO LB film, the main absorption band at 567 with a small shoulder at 525 nm were detected. Absorption spectra of OX4/ODTMA at the Sum sub-phase were dominated by the main band at 623 nm attributed to the monomeric form with a small shoulder at 580 nm, assigned to molecular aggregates. Consequently, the two dye component LB film (RhBO/OX4/ODTMA) in a Sum sub-phase exhibited two absorption bands attributed to the monomers of RhBO (567 nm) and OX4 (623 nm), respectively. Detected absorbance in all cases was very low (e.g. 0.008 a.u.), which is explained by the formation of a very thin (monomolecular) film.

In Fig. 3 are shown the emission spectra of LB films based on individual dyes and two dye components (RhBO/OX4/ODTMA) in a Sum sub-phase after the excitation at 500 nm. The black line corresponds to the emission from RhBO and the green line to the emission from Ox4/ODTMA in a Sum sub-phase. In all the cases the excitation wavelength was selectively chosen for the emission of RhBO molecules. For that reason we see a small intense emission from Ox4 molecules. The red line corresponds to the LB film based on two dye components. As we can see the emission from RhBO molecules, the fluorescence of this dye was significantly quenched in favour of high intense emission band from Ox4 molecules. One can conclude that RET occurred in the film formed from two dyes components. The cations of RhBO played the role of molecular antennas absorbing green light at the beginning of the process. Quenching of light emission from rhodamine (580 nm) in favour of the red light luminescence from oxazine (635 nm) proceeded as non-radiative RET.
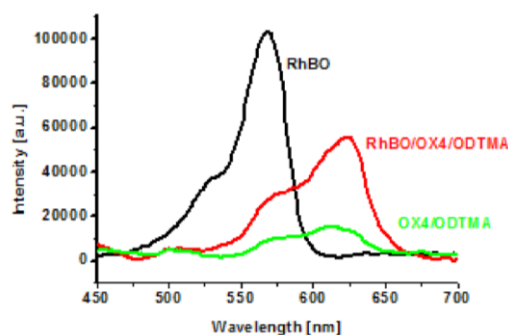

Fig. 3 – Emission spectra for LB films of the individual dye cations at the Sum subphase (RhBO, black line, OX4/ODTMA green line) and for the two dye component LB film (RhBO/OX4/ODTMA) at the Sum sub-phase (red line). The excitation at 500 nm was performed

5. CONCLUSIONS

The energy transfer process between two dye cations was efficiently achieved at the Sum sub-phase in Langmuir-Blodgett films. The crucial problem was to suppress the dye cationic aggregation contributing to the energy transfer to non-luminescent species and overall fluorescence quenching. A partial reduction of the molecular aggregates was accomplished by the incorporation of long-chain alkylammonium cations in the systems. Moreover, the presence of the surfactants played a necessary role in the formation of hybrid assemblies, the precursors for Langmuir-Blodgett films.

6. ACKNOWLEDGEMENTS

the project implementation: Centre for materials, layers and systems for applications and chemical processes under extreme conditions - Stage II

REFERENCES

1. M. Ogawa, K. Kuroda *Chem. Rev.* **95**, 399 (1995).
2. C. Sanchez, B. Lebeau, F. Chaput, J-P. Boilot, *Adv. Mat.* **15**, 1969 (2003).
3. C. Sanchez, B. Julián, P. Belleville, M. Poppal, *J. Mat. Chem.* **15**, 3559 (2005).
4. G. Schulz-Ekloff, D. Wohrleb, B. van Duffel, R.A. Schoonheydt, *Microporous Mesoporous Mat.* **57**, 91 (2002).
5. V. Ramamurthy, K.S. Schanze *Solid State and Surface Photochemistry, vol. 5, Molecular and Supramolecular Photochemistry* (Dekker, New York: 2000).
6. J.R. Lakowicz, in: Principles of Fluorescence Spectroscopy (New York: Lkuver Academic-Plenum: 1999).
7. A.R. Mermut, *Layer Charge Characteristics of 2:1 Silicate Clay Minerals, CMS Workshop Lectures Vol. 6* (Colorado: The Clay Minerals Society, Boulder: 1994).
8. J. Bujdák, N. Iyi, T. Fujita, *Clay Miner.*, **37**, 121 (2002).
9. J. Cenens, R.A. Schoonheydt, *Clays Clay Miner.* **36**, 214 (1988).
10. L. Antonov, G. Gregor, V. Petrov, M. Kubista, J. Nygren, *Talanta*, **49**, 99 (1999).
11. T. Kobayashi, *J-aggregates* (Singapore: World Scientific: 1996).
12. R. Sasai, N. Iyi, T. Fujita, V.M. Martínez, K. Takagi, H. Itoh, *Langmuir,* **20**, 4715 (2004).
13. R. Sasai, T. Itoh, N. Iyi, K. Takagi, H. Itoh, *Chem. Letter*, **34** 1490 (2005).
14. A. Czímerová, J. Bujdák, N. Iyi, *J. Photochem. Photobiol. A*, **187**, 160 (2007).
15. A. Czímerová, N. Iyi, J. Bujdák, *J. Colloid Interface Sci.*, **306**, 316 (2007).
16. A. Czímerová, N. Iyi, J. Bujdák, *J. Colloid Interface Sci.*, **320**, 140 (2008).
17. A. Czímerová, J. Bujdák, R. Dohrmann, *Appl. Clay Sci.*, **34**, 2 (2006).
18. A. Ulman, *An introduction to ultrathin organic films: From Langmuir-Blodgett films of self assemblies* (New York: Academic Press: 1991).
19. R.H.A. Ras, B. van Duffel, M. Van der Auweraer, F.C.De Schryver, R.A. Schoonheydt, *Proceedings of the 12th International Clay Conference, Bahía Blanca, Argentina*, 473 (2001).
20. S.A. Hussain, S. Chakraborty, D. Bhattacharjee, R.A. Schoonheydt*, Spectrochimica Acta A*, **75**, 664 (2010).