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One – and Two-Step Resonance Energy Transfer Between Cyanine Dyes in Layered Silicates Colloidal Systems

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Resonance energy transfer (RET) is of high interest for both the basic research and practical applications. It is a phenomenon of radiationless transmission of energy between donor and acceptor molecules. In this study single- and two-step (RET) was investigated between cyanine dye cations (NK1, NK2, NK3) in colloids of layered silicate, synthetic Sumecton saponite. In these systems the dye molecules played role of the energy donors (NK1) or energy acceptors (NK2, NK3) or both (NK2). The adsorption and formation of various types of dye species was studied using visible spectroscopy. The absorption spectroscopy did not detect any significant molecular aggregation of the dyes at the surface of saponite particles. The RET process was described by fluorescence spectroscopy. Both the single- and two-step RET were detected in saponite dispersion. Effects of various parameters on the efficiency of the RET process, such as dye concentrations, saponite properties the distances between co-adsorbed dye cations were found to be essential.

Keywords: Resonance energy transfer, Smectites, Cyanine dyes, Fluorescence spectroscopy.

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1. INTRODUCTION

Hybrid materials based on organic dyes and layered silicates, such as smectite, are interesting due to their potential applications in photochemistry and photophysics [1 – 3]. Smectites are composed from microscopic particles of nanometer thickness. Due to the isomorphic substitutions in their structure, smectite layers bear a negative charge. The charge is compensated by hydrated inorganic cations, which can be easily exchanged, for example, for organic dye cations [4]. Besides the adsorption, molecular aggregation of the cationic dyes often occurs and it significantly affects the optical properties of the organic dyes [5]. If two different dye molecules are in distances comparable to or smaller than Förster radius (1 – 10 Å) and absorption spectrum of the first dye significantly overlaps with emission spectrum of the second one, resonance energy transfer (RET) may occur [6]. In this process the interacting dye molecules played role of the energy donors (ED) or energy acceptors (EA) [7]. RET can be monitored as the reduction of ED light emission and excited lifetimes and to the increase in light emission from EA [8].

The objective of this work was to characterize one - and two-step resonance energy transfer between three cyanine dyes in colloidal systems of layered silicates.

2. EXPERIMENTAL METHODS

2.1 Materials

A synthetic saponite Sumecton (Kunimine Ind. Co) (Sum) was used in this study. The structural formula of the Sum is as follows: $Na_{0,94}Mg_{0,14}[(Si_{7,20}Al_{0,80})O_{20}(OH)_4]$ and the cation exchange capacity of Sum is 0.87 ± 0.05 mmol·g^{-1} [9]. The cationic cyanine dyes NK 863 (N1), NK 88 (N2) and NK 737 (N3) were purchased from Sigma Aldrich. The molecular structures of used dyes are depicted in Fig. 1. Sumecton and the dyes were used without further purification. Colloids containing a single dye (Sum/N1, Sum/N2, Sum/N3), a pair of the dyes (Sum/N12, Sum/N13 and Sum/N23) and all three dyes (Sum/N123) were prepared. The final concentration and loading of the dyes solutions in the dispersions were 1×10^{-6} M and 0.05 mmol·g^{-1} of smectite, respectively.

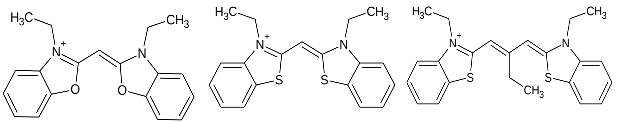
N1 N2 N3

Fig. 1 – Molecular structures of cyanine dyes

2.2 Experimental procedures

The absorption spectra of dispersions were measured using spectrophotometer Varian, (CARY 100) 1 min and 24 h after preparation. The spectra of smectite dispersions without dye, related to light scattering, were subtracted from the spectra of dye/smectite dispersions to obtain the pure spectra of dye species. The emission spectra were obtained using fluorescence spectrophotometer FluoroLog (Horiba, Jobin Yvon). The excitation was performed at 370 nm for all measurements to excite N1 cations selectively. Under these conditions, RET can be characterized as the reduction of light emission from ED in favour of the fluorescence from EA.

3. RESULTS AND DISCISSION

3.1 Absorption spectra of cyanine dyes in saponite dispersion

Fig. 2 shows absorbance spectra of the cyanine dyes ethanol solutions and their mixture in Sum

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dispersions. Changes in the absorption spectra due to the presence of Sum were observed in the case of N2 and N3 dyes (Fig. 2). Absorption band corresponding to the monomeric forms of N2 at 425 nm decreased in favour of small shoulder at 402 nm corresponding to dye dimers. Similar change occurred in the case of N3. The changes are probably due to the molecular aggregation of dyes in colloidal systems [10]. Dimerization of both the N2 and N3 was detectable also in two-and three-component systems (Fig. 3). Nevertheless, molecular aggregation was relatively low in all studied systems.

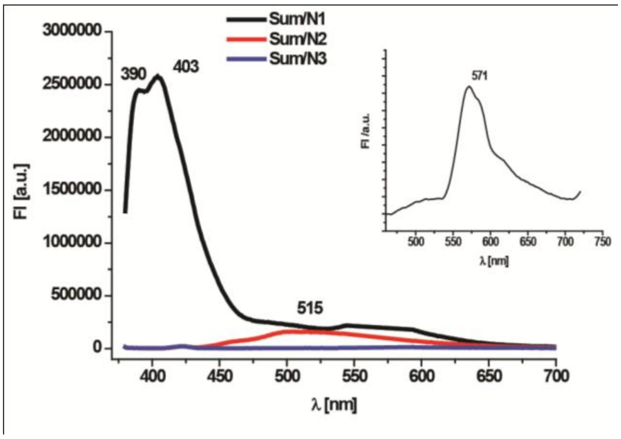

Fig. 2 – Absorption spectra of dyes N1, N2, N3 and their mixture in ethanol (a) and Sum dispersion (b) measured 1 minute after the addition of dye

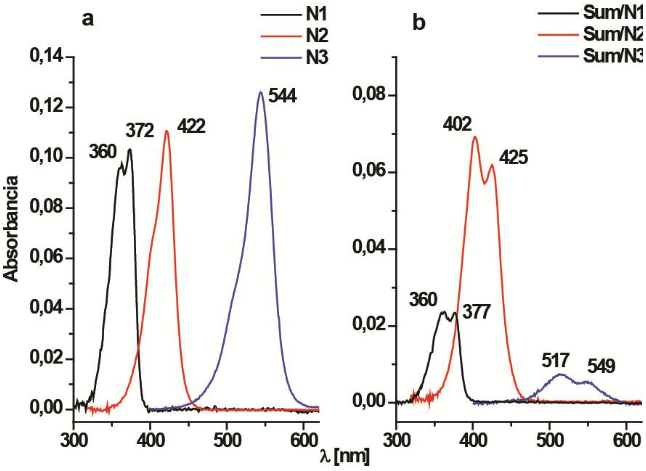

Fig. 3 – Absorption spectra of mixed systems consisting of N1, N2, N3 in the Sum dispersion.

3.2 Fluorescence spectra of dyes in saponite dispersion

Fig. 4 shows the emission spectra of simple systems of the cyanine dyes in the Sum dispersion. Emission spectra were measured after the selective excitation of N1 at 370 nm. Only weak emission was detected for N2 / Sum system and almost none for N3 / Sum. The inserted figure shows the strong emission peak at 571 nm for the system N3 / Sum after selective N3 dye excitation (450 nm).

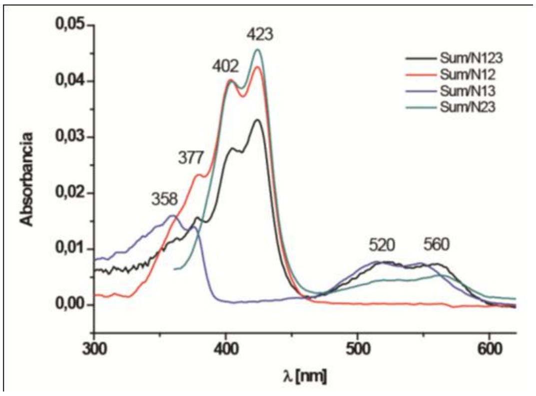

Fig. 4 – Emission spectra of cationic dyes N1, N2 and N3 in the Sum dispersion. Excitation at 370 nm. Inside image is embedded emission spectrum of N3 dye Sum dispersion after excitation at 450 nm

Emission spectra of Sum dispersions containing a pair of the dyes are shown in Fig. 5. For N13 / Sum, two strong emission bands were observed: A pair of the band at 390 and 403 nm, corresponding to the monomer and dimer of N1 and one at 585 nm assigned to N3 monomers. A small spectral overlap between ED and EA molecules enables only less efficient RET reflected in a lower emission from N3. More efficient RET occurred in the emission spectra of systems N12 / Sum and N23 / Sum, which can be explained by larger spectral overlap between these pair of the dyes. There was the increase of the emission of the energy acceptor molecules (either N2 or N3); which is an evidence for energy transfer.

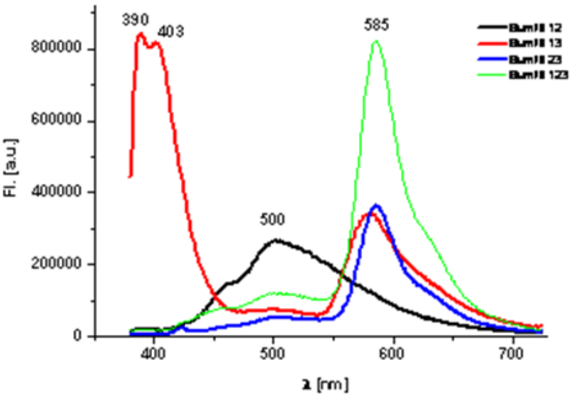

Fig. 5 – Emission spectra of mixed systems consisting of N1, N2, N3 in the Sum dispersion. Excitation at 370 nm

Fig. 5 shows also the spectrum of a three-dye component system (N123 / Sum). The emissions from N1 and N2 dyes playing the role of ED (bands at 450 and 500 nm) are substantially reduced. The fluorescence at 585 nm significantly increased, which is an evidence for efficient RET, likely occurring in two steps: Initially most efficiently excited N1 cations transfer their energy to N2, playing the role of EA in this step. Excited N2 cations are then quenched and transfer energy to N3 molecules. The emission of N3 substantially increased and those N1 and N2 molecules were significant reduced.

4. CONCLUSIONS

This paper studied one - and two-step resonance energy transfer between three cyanine dyes in layered silicates colloidal systems. Absorption spectroscopy confirmed only a low extent of dye aggregation process. Fluorescence spectroscopy has proven RET in Sum dispersions. Energy transfer in colloidal systems occurs due to the concentration of dye molecules on the surface of smectite colloidal particle.

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