



## Research paper

## Unique solvatochromism of cyanine/saponite hybrid systems

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## ABSTRACT

The present study is primarily focused on the investigation of spectral properties of cationic cyanine dye (1,1'-diethyl-4, 4'-carbocyanine iodide, denoted as "NK5") adsorbed into the structure of synthetic clay mineral (Sumecton SA, denoted as "SUM") as a host matrix. The hybrid systems were investigated by means of absorption and fluorescence spectroscopy. Beside the solvent effect, the influence of dye/saponite ratio on the formation of specific dye species was studied in detail. It was found that used solvents have greatly affected the spectral properties of prepared hybrids. The NK5/saponite systems in ethanol and methanol were dominated by isolated dye cations. In the NK5/saponite systems in acetone and acetonitrile, the formation of higher aggregates was significantly suppressed. Moreover, the fluorescence spectra showed evidence of the formation of highly fluorescent *J*-aggregates. Finally, the fluorescence quantum yields of the NK5/saponite systems in various solvents were calculated. It was found that polar protic solvents as ethanol and methanol could stabilize the hybrid cyanine/saponite system with higher quantum yields as in case of used aprotic solvents.

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## 1. Introduction

Cyanine dyes came into the spotlight in 1856 for their potential practical applications as a light sensitizers to silver halide emulsions in a region of the spectrum to which the silver halide is normally not sensitive (Williams, 1856). Besides their applications in photography over many years, these dyes can be found in a wide range of applications such as industrial paints, probes for biological activity, trapping of solar energy, light harvesting systems, in photodynamic therapy as potential sensitizers, etc. (Shindy et al., 2016; Ferreira et al., 2015; Moreira, 2015; Solomon, 2014; Keisar et al., 2014; Zhang et al., 2012; James, 1997; Chibisov and Gornor, 1997; Krieg and Edmond, 1993). The generic cyanine dyes consist of two nitrogen centers, one of which is positively charged and linked by a conjugated chain of an odd number of carbon atoms to the other nitrogen (Behera et al., 2007). Generally, these dyes have all-trans geometry in their stable forms. Many of them usually undergo photoisomerization (Nair and Penzkofer, 1981; Baumler and Perzkofer, 1990; Tocho et al., 1992).

Cyanine dyes – as many other dyes – are held together via intermolecular van der Waals attractive forces. Generally, they can self-associate in a solution or at the solid-liquid interfaces, which is a very important phenomenon in dye chemistry (Bergman and O'Konski, 1963; Yariv and Lurie, 1971; Breen and Loughlin, 1994; Arbeloa et al., 1996; Bujdák et al., 2002; Czímerová et al., 2004). The formed aggregates are usually characterized by spectral changes in absorption/fluorescence

spectra with respect to the monomeric species. From the observed spectral shifts in the visible region, one can distinguish between two main forms of dye aggregates. The first one is represented by a sandwich-type *H*-dimers and/or higher aggregates which generally absorb light at higher energies with respect to monomers. Cyanine dyes can also form highly ordered self-assemblies, commonly known as *J*-aggregates, characterized by a narrow band at lower energies with respect to monomeric dye forms (Jelly, 1936; Scheibe, 1937). These aggregates exhibit a delocalized excitation which is the result of the exciton formation. The above mentioned phenomena, i.e. excitation and exciton formation of cyanine dyes, play an important role in many fundamental and biological processes, mainly related to light harvesting and transport of electrons and energy in such kind of processes (Eisfeld and Briggs, 2006). Moreover, different types of intermolecular forces such as hydrogen bonding,  $\pi$ - $\pi$  stacking will be taken into consideration in the formation of supramolecular structures. Among these non-covalent interactions,  $\pi$ - $\pi$  stacking plays an important role in the self-assembly of cyanine dyes and can affect the formation of aggregates.

There have been numerous works dealing with the relationship between the structure and spectral properties of *J*-aggregates (Kobayashi, 1996 and references therein). Many theoretical analyses suggest that the position and line shape of the *J*-band are sensitive to the regularly arranged molecular geometry.

Hence, a small change in the environment or reaction conditions (e.g. solvent effects, incorporation of dye molecules into the inorganic matrix) can affect the formation of *J*-aggregates with different molecular structure and with different spectral properties (Würthner et al., 2011). Generally, the aggregates absorbing light at higher energies are

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not fluorescent. Hence, these aggregates represent an undesirable component when constructing a photofunctional hybrid materials. On the other hand, *J*-aggregates of dyes represent a fluorescent species. The *H*-dimers and *H*-aggregates are quite common for all types of dyes, but *J*-aggregates are mostly known for cyanine dyes.

The tendency of dye molecules to form aggregates depends on the concentration of the dye, pH of the environment, ionic strength, temperature and solvent polarity. One of the most promising routes to suppress the undesired *H*-aggregation and to enhance the formation of *J*-aggregates is the incorporation of dye molecules to the structure of inorganic layered materials. In this context, layered silicates from a smectite group are the right candidates of choice. Smectites are layered clay minerals whose layers bear a negative charge due to the isomorphous substitutions in their structure. This negative charge is compensated by hydrated inorganic cations at the surface and in the interlayer space of smectites. These inorganic cations can be easily exchanged for organic ones via an ion-exchange reaction (Newman, 1987). In this context, the right choice of smectite with suitable properties (e.g. sufficient surface for the adsorption, layer charge, concentration of the smectite dispersion) is the key factors to enhance the fluorescent properties of resulting hybrid materials.

In this work, the cyanine dye “NK5” and a smectite sample, saponite Sumecton (SUM) were utilized. The main idea of this work was to study the spectral behaviour of the NK5 dissolved in four different solvents in order to study the solvatochromic effect. Moreover, the adsorption of NK5 dissolved in different solvents on the layered structure of saponite was studied in detail. The main goal of this work was to prepare a photofunctional hybrid materials containing NK5 with enhanced fluorescent properties.

## 2. Experimental

### 2.1. Materials

A synthetic saponite Sumecton SA (SUM) from the Kunimine Ind. Co. was used in this study. SUM is a trioctahedral, very pure synthetic saponite, characterized by very small particles and the ability to form well dispersed and stable colloids in water (Takagi et al., 2002a; Takagi et al., 2002b). This material was chosen due to the lack of the iron in the structure and its optimal layer charge. The layer charge is an intrinsic property of clay mineral surface and significantly affects the adsorption and dye aggregation and hence the absorption and fluorescence properties. Low negative charge is an essential parameter for preventing larger extents of the molecular aggregation of cationic dyes. The size of the negative layer charge was determined by calculation of the cation exchange capacity, which is  $0.87 \pm 0.05$  mmol/g (Czimerová et al., 2006).

The cationic cyanine dye 1,1'-diethyl-4, 4'-carbocyanine iodide (NK5) was purchased from Lambda Physik GmbH (Göttingen, Germany) and was used as received. The molecular structure of NK5 is depicted in Fig. 1. The highest-grade solvents, i.e. ethanol (EtOH), methanol (MeOH), acetone (ACT) and acetonitrile (ACN) were purchased from Merck KGaA, Germany.

### 2.2. Methods

#### 2.2.1. Preparation of NK5 solutions with various solvents

Dye solutions were prepared using 4 different solvents, namely EtOH, MeOH, ACT and ACN for the study of solvent effects on the luminescent spectra. The final concentration of dye varied from

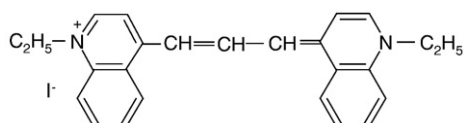


Fig. 1. Molecular structure of NK5 dye.

$1 \times 10^{-3}$  mol·dm<sup>-3</sup> to  $1 \times 10^{-7}$  mol·dm<sup>-3</sup>. The absorption and fluorescence spectra were recorded after preparing the NK5 solutions.

#### 2.2.2. Preparation of SUM/NK5 dispersions

For a preparation of SUM dispersions, the ultrapure water Type 1 (Millipore SYNERGY/DIRECTQ® 3UV, 5UV, 8UV Ultrapure water system) was used. SUM dispersions, ultrapure water and NK5 solutions in various solvents were mixed in order to obtain dispersions with final NK5/SUM ratios of 0.01; 0.02; 0.05; 0.10; 0.20 and 0.50 mmol/g. The final concentration of NK5 in dispersions was kept constant at  $5 \times 10^{-6}$  mol·dm<sup>-3</sup>, hence the dye/saponite ratio was adjusted by the amount of saponite.

#### 2.2.3. UV/vis measurements

The absorption spectra of prepared dye solutions and SUM/NK5 dispersions were recorded using a Cary 5000 Varian Inc. UV/Vis spectrophotometer. In case of SUM/NK5 dispersions the spectra were recorded 1 min after mixing the components. The spectra of pure SUM dispersions (without NK5 solutions) were subtracted from their SUM/NK5 counterparts to eliminate the effect of light scattering on saponite colloidal particles. The absorption spectra were recorded in a range of 200–800 nm.

#### 2.2.4. Fluorescence measurements

Steady-state fluorescence spectra were recorded using a Fluorolog FL 11 (Horiba Yobin Ivon, Japan) fluorescence spectrophotometer upon excitation at 520 nm.

The fluorescence quantum yield (FQY) of the NK5 solutions in different media and of SUM/NK5 hybrid systems were calculated using the formula:

$$\Phi = \Phi_{ref} \frac{n^2}{n_{ref}^2} \frac{I A_{ref}}{I_{ref} A} \quad (1)$$

where  $\Phi$  and  $\Phi_{ref}$  denote fluorescence quantum yield of sample and reference,  $n^2$  and  $n_{ref}^2$  denote refractive indices of environments (i.e. 1.36 for EtOH, 1.33 for MeOH, 1.36 for ACT, 1.34 for ACN (Snyder et al., 1997), and 1.6 for water dispersion of SUM (Hsu, 1999)).  $I$  and  $I_{ref}$  represent integrated fluorescence intensity of sample and reference,  $A$  and  $A_{ref}$  represent the absorbance values of sample and reference at the excitation wavelength (Lakowicz, 1999).

## 3. Results and discussions

### 3.1. Absorption spectra of NK5 solutions with various solvents

The absorption spectra of NK5 were measured for three different concentrations, i.e.  $1 \times 10^{-5}$  mol·dm<sup>-3</sup>,  $1 \times 10^{-6}$  mol·dm<sup>-3</sup> and  $1 \times 10^{-7}$  mol·dm<sup>-3</sup> (depicted in Supplementary data section, Fig. 1). Absorption spectra of NK5 in four different solvents show rather similar features. The main absorption band of NK5 in EtOH at 710 nm is attributed to a monomeric dye form. Slight shift was observed in MeOH (706 nm), in ACT (704 nm) and in ACN (to 708 nm). The intensity of main band at concentration  $1 \times 10^{-5}$  mol·dm<sup>-3</sup> slightly increased in order from ACT, MeOH, ACN to EtOH. Accordingly, with decrease of the concentration of solutions, the intensity of the main band decreased. Also, a very low absorption was detected in case of NK5 solutions with a concentration of  $1 \times 10^{-7}$  mol·dm<sup>-3</sup>.

### 3.2. Absorption spectra of SUM/NK5 dispersions

UV/vis spectroscopic analysis was performed for the study of interaction between NK5 in various solvents with synthetic saponite SUM. SUM has a very low particle size, the particles are easily dispersed in water and a layered structure can be easily exfoliated. In this study, 6 loadings were used. The ratio of n(NK5)/m(SUM) was modulated to

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