



Research paper

# Spectral behaviour of TMPyP/layered silicate hybrid nanomaterials in aqueous dispersions of reduced-charge montmorillonites



A. Čeklovský\*, P. Boháč, A. Czímerová

Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, 845 36 Bratislava, Slovakia

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## ABSTRACT

Spectral properties of tetracationic organic dye, *meso*-tetrakis(*N*-methylpyridinium-4-yl) porphyrin adsorbed on layered silicate templates of various layer charge were investigated. A series of reduced charge Nanocor montmorillonites was used as host matrices. The study primarily focuses on the influence of the layer charge on the emission characteristics and photoactivity of prepared materials. Usually, adsorption of dyes such as porphyrins leads to significant changes in their spectral characteristics with the main goal being the preservation of their photoactivity. The spectral changes can be explained in terms of e.g. structural changes (flattening, protonation), as well as molecular aggregation. Hence, the aim of this study is to clarify the way to influence the spectral properties and the subsequent photoactivity of incorporated molecules via a strategy of appropriate combination of a photoactive component with specific inorganic templates.

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## 1. Introduction

Hybrid organo-inorganic nanomaterials have attracted much attention of material scientists for their unique and interesting properties, different from those of components from which they are composed of. In our work, the inorganic component of nanocomposites is represented by clay minerals from the smectite group. These are widely known for their versatile, modifiable and advantageous properties, such as swelling, formation of stable colloids, large surface area and especially their capacity to adsorb not only inorganic but also organic compounds (van Olphen, 1977; Newman, 1987). These, but also many other properties provide a great basis for the development of novel functional organic/inorganic nanocomposites, with clay mineral as an inorganic carrier (Fig. 1). The formation of the hybrid materials composed of clay minerals and organic compounds can be easily controlled via the process of ion-exchange, intercalation or adsorption, resulting in various structural forms of nanomaterials (Ogawa and Kuroda, 1995; Shichi and Takagi, 2000; Takagi et al., 2006; Takagi et al., 2013). Up to the present, the interaction between layered inorganic materials and

organic chromophores has been the subject of numerous studies (Chernia and Gill, 1999; Dias et al., 2000; Takagi et al., 2002a, 2002b; Schulz-Ekloff et al., 2002; Bujdák et al., 2003a, 2003b, 2003c; Sanchez et al., 2003; Sasai et al., 2004; Eguchi et al., 2004; Schalley et al., 2004; Bujdák, 2006; Čeklovský et al., 2009a, 2009b; Takagi et al., 2010). One of the most significant phenomena occurring for such systems are formation of dye molecular assemblies and the changes of spectral properties of adsorbed chromophores (Bujdák and Komadel, 1997; Bujdák et al., 2001; Bujdák et al., 2003a, 2003b, 2003c; Ishida et al., 2012).

Nowadays, the photofunctional properties of hybrid dye systems have recently been investigated in detail due to their potential applications (Takagi et al., 2002a, 2002b; Bujdák and Iyi, 2005; Čeklovský et al., 2008; Czímerová et al., 2008). The study of the photoprocesses of organic photoactive compounds can lead to a wide variety of useful applications in photochemically controlled reactions, construction of molecular devices for optics, solid-state lasers, photodynamic therapy of cancer, etc. Moreover, understanding of abovementioned processes can be useful in the preparation of photoactive materials with modifiable and desirable properties (Arbeloa et al., 1996; Sanchez et al., 2005).

This work is focused on the investigation of hybrid systems based on clay mineral colloids and porphyrin dye cations. The spectral properties of aqueous colloidal dispersions were the subject of study, with the

\* Corresponding author.

E-mail address: [alexander.cekvovsky@gmail.com](mailto:alexander.cekvovsky@gmail.com) (A. Čeklovský).

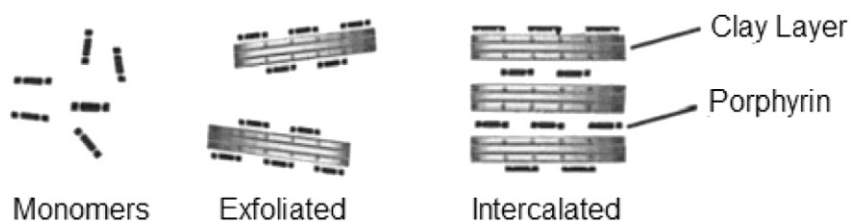


Fig. 1. The structural image of hybrid clay/porphyrin complexes.

impact on optical properties of adsorbed porphyrin cations. The strategy of the combination of phenomena based on porphyrin adsorption and controlling a layer charge of inorganic host leads to the formation of novel photofunctional structures and arrangements with desirable and interesting spectral properties.

## 2. Experimental

### 2.1. Materials

Montmorillonite Nanocor (Nanocor Inc., USA) was used for the preparation of the series of layered silicates called reduced charge montmorillonite (RCM). The structural formula of Nanocor (Czimerová et al., 2006) is  $\text{Na}_{1.31}[(\text{Si}_{7.47}\text{Al}_{0.53})(\text{Al}_{2.68}\text{Fe}_{0.42}\text{Mg}_{0.95})\text{O}_{20}(\text{OH})_4]$ . The presence of low amount of iron in octahedral sheet has no influence on spectral properties of hybrids. *Meso*-tetrakis(*N*-methylpyridinium-4-yl) porphyrin was purchased from Livchem, Germany, and was used as received. For a preparation of layered silicate dispersions, the ultrapure water Type 1 (Millipore SYNERGY/DIRECT-Q® 3UV, 5UV, 8UV Ultrapure water system) was used.

### 2.2. Methods

$\text{Li}^+$ -saturated montmorillonite was heated at various temperatures (60–200 °C, Table 1) for 24 h. Thermal treatment induced the migration and fixation of  $\text{Li}^+$  cations into the layers. The layer charge reduction increased with increasing preparation temperature, as shown by the cation exchange capacity (CEC) values in Table 1. The CEC was determined by an ion-exchange reaction with barium chloride solution as reported elsewhere (Czimerová et al., 2006). The dispersions of Nanocor series were mixed with deionized water and aqueous TMPyP solutions ( $c = 1 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$ ) to reach the porphyrin/silicate loading of 10% vs. CEC.

The absorption spectra were recorded 1 min and 48 h after the addition of porphyrins using a Cary 5000 Varian UV–vis spectrophotometer. The spectra of the pure clay mineral dispersions (without porphyrins) were subtracted from their clay mineral-porphyrin counterparts to eliminate the effect of light scattering on montmorillonite colloidal particles. Steady-state fluorescence spectra and excitation spectra were recorded using a Fluorolog FL11 luminescence spectrophotometer upon excitation at 450 nm.

The fluorescence quantum yield (FQY) of individual hybrid systems was calculated using the formula

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

Table 1

CEC values of reduced charge montmorillonite;  $\sigma$  denotes standard deviation (Czimerová et al., 2006; Czimerová et al., 2008).

Sample	N60	N100	N110	N120	N130	N140	N150	N200
CEC (mmol/g)	1.35	1.24	1.18	1.14	1.05	0.95	0.75	0.49
$\sigma$	0.05	0.03	0.02	0.04	0.03	0.03	0.02	0.05

where  $\Phi$  and  $\Phi_{ref}$  denote fluorescence quantum yield of sample and reference,  $\eta^2$  and  $\eta_{ref}^2$  denote refractive indices of environments (i.e. 1.3 for water and 1.6 for silicates) (Jyh-Ping Hsu, 1999),  $I$  and  $I_{ref}$  represent integrated fluorescence intensity of sample and reference,  $A$  and  $A_{ref}$  represent the absorbance values at the excitation wavelength.

## 3. Results and discussion

### 3.1. Absorption spectra

Fig. 2 depicts the absorption spectra of TMPyP in aqueous dispersions of Nanocor montmorillonite specimens with different layer charge. The experiments were performed at the same dye loading 10% vs. CEC. This dye loading was chosen due to the following assumptions: i.) At this loading level, the possible undesirable phenomena such as aggregation, inner filter effects, or others can be effectively ruled out. ii.) Sufficiently high molar extinction coefficient of TMPyP allows to perform a precise and exact spectral properties determination in very low concentration ranges.

The absorption maximum of TMPyP solution is at 421 nm. For TMPyP, the spectral bands of N60–N130 systems are consistently shifted from 421 to ~450 nm. This bathochromic shift is assigned to the “flattening effect” of the porphyrin adsorption on layered silicate surface. This effect is caused by a rotation of methylpyridyl groups upon adsorption on clay mineral surface (Chernia and Gill, 1999). The continual decrease of absorption intensities can be observed, while the dye loading is different in each sample in terms of keeping the 10% vs. CEC loading condition (see Table 1). Moreover, a band broadening due to the enhanced light scattering might be the consequence of lower colloidal stability of the systems with N140 to N200.

However, the spectral behaviour in case of sample N200 is completely different if compared to its counterparts with higher layer charge. As can be seen, the absorption spectra of N200 are facing a drastic decrease in absorption intensity, as well as an extensive band broadening. This phenomenon can be attributed to a significantly lower

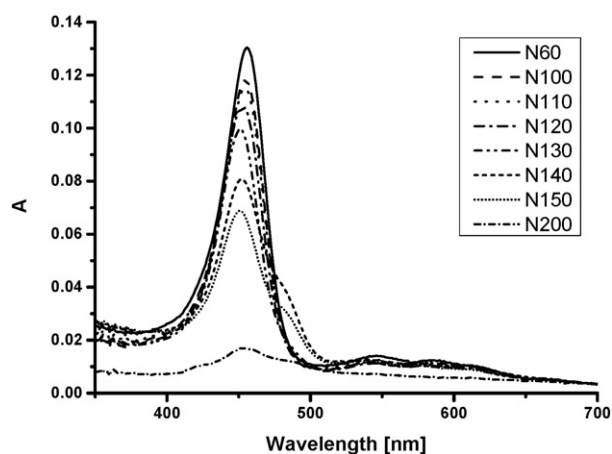


Fig. 2. Absorption spectra of TMPyP in aqueous dispersions of Nanocor montmorillonite systems. TMPyP loading = 10% vs. CEC.

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