Journal of Colloid and Interface Science 324 (2008) 240–245

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

# Spectral properties of TMPyP intercalated in thin films of layered silicates

A. Čeklovský [*], A. Czímerová, M. Pentrák, J. Bujdák

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

ARTICLE INFO

*Article history:*
Received 17 March 2008
Accepted 29 April 2008
Available online 2 June 2008

*Keywords:*
Layer charge
Clay minerals
Porphyrin
Smectites
Fluorescence spectroscopy
Visible spectroscopy
Intercalation

ABSTRACT

The objective of this study was to investigate the spectral characteristics of tetracationic porphyrin dye (TMPyP), intercalated into films of three smectites. The smectites represented the specimens of high (Fluorohectorite; FHT), medium (Kunipia F montmorillonite; KF), and low layer charge (Laponite; LAP). Intercalation of TMPyP molecules was proven by XRD measurements. The molecular orientations of the dye cations were studied by means of linearly polarized ultraviolet–visible (UV–vis) and infrared (IR) spectroscopies. Both the UV–vis and the IR spectroscopy proved the anisotropic character of the films. The spectral analysis of the polarized UV–vis spectra and consequent calculations of tilting angles of the transition moments in the region of Soret band transitions were in the range of 25–35°. The determined angles indicated that the molecular orientation of the dye cations was almost parallel to the surface of the silicates. Slightly higher values, determined for a FHT film, indicated either a slightly more tilted orientation of the dye cations or the change of molecular conformation after the intercalation of the dye. Quenching of TMPyP fluorescence was observed, resulting from the formation of bimolecular layer arrangements with sandwich-type assemblies of the dye molecules.

© 2008 Elsevier Inc. All rights reserved.

## 1. Introduction

Investigation of the interaction between host layered inorganic matrices and the organic guest chromophores has been the subject of numerous studies [1–8]. Intercalation of organic dyes into layered inorganic solids can lead to the formation of novel materials with superior properties. Specific interactions of organic dyes with inorganic surfaces often lead to chemical and thermal stabilization of the guest molecules, dye molecules' self-assembly, and control of the molecular orientations of the chromophores. The distribution and orientation of adsorbed organic species can be controlled by the interactions between the surface of inorganic solids and the adsorbent. The presence of coadsorbed species or modifier as the third component may significantly influence the optical properties of adsorbed organic chromophores [9,10].

Photofunctional properties are one of the most promising properties of dye supramolecular systems, which can be used in various applications [11]. Therefore, study of the photophysical and photochemical processes of organic photoactive species can lead to a wide variety of applications in such areas as reaction media for controlled photochemical reactions or in construction of devises for optics, memory storage devices, etc. [12].

Generally, dye molecules tend to aggregate on the clay mineral surface or in the interlayer spaces. The layer charge of layered silicates controls the molecular aggregation of the dyes of various structural types [13,14]. The occurrence of molecular aggregation is considered to be a serious problem during the preparation of luminescent hybrid materials, based on organic dyes embedded in inorganic solid hosts [15], because it leads to decreasing of the excited state lifetimes of photoactive species.

In this study, we focused on investigation of the spectral behavior of tetracationic porphyrin 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)porphyrin (TMPyP), intercalated in the layered silicate matrices with various layer charge. The effect of the layer charge of silicate hosts is expected to play an important role, both in modifying the optical properties of embedded TMPyP and also the molecular orientation of TMPyP species on a silicate surface.

## 2. Experimental

### 2.1. Materials

In this study we used Fluorohectorite (FHT), $Na^+$-saturated montmorillonite Kunipia F (KF), and $Na^+$-saturated hectorite Laponite RD (LAP) as representative layered silicates of high, medium, and low layer charge densities, respectively. Synthetic trioctahedral silicates FHT and LAP were obtained from Corning Inc. (New York) and Laporte Industries Co. (UK), respectively. Dioctahedral KF was purchased from Kunimine Industries Co. (Japan) and is of natural origin. The CEC values represent the amount of cations that compensate the negative layer charge and are listed in Table 1. The tetra-*p*-tosylate salt of TMPyP (Scheme 1) was obtained from Frontier Scientific Europe, Ltd. (UK), and was used as received. Quartz slides (1 × 1 inch) were obtained from SPI Supplies (PA). The slides were transparent in a UV–vis region at wavelengths above 200 nm.

---

[*] Corresponding author.
*E-mail address:* alexander.ceklovsky@gmail.com (A. Čeklovský).

0021-9797/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcis.2008.04.073

**Table 1**
CEC values of clay mineral samples

| Sample | CEC ($\text{mmol g}^{-1}$) | $\sigma$[a] |
|---|---|---|
| FHT | 1.48 | 0.03 |
| KF | 1.24 | 0.09 |
| LAP | 0.78 | 0.03 |

[a] $\sigma$ denotes standard deviation.

### 2.2. Methods

Quartz slides were treated using Piranha solution, 7:3 (v/v) mixture of concentrated $H_2SO_4$, and 35% $H_2O_2$ for 30 min at 90 °C in order to hydrophilize the surface and to remove the organic residues and impurities. Water suspensions of layered silicates were prepared by mixing 0.5 g sample/50 ml water with consequent ultrasonic disaggregation treatment for 30 min. Oriented thin films of layered silicates were prepared by covering the surface with suspensions and dried at room temperature. Dried films were immersed into the solution of TMPyP ($c = 10^{-3}\ \text{mol dm}^{-3}$) and the system was equilibrated for 6 h. Prepared films were washed with water and dried at room temperature.

X-ray diffraction patterns were recorded on diffractometer Bruker D8 Discover (Cu$K\alpha$ radiation, 40 kV/30 mA).

Polarized UV–vis absorption spectra of thin films were recorded in the region 350–700 nm by a Cary 100 Varian UV–vis spectrophotometer using a Glan-Taylor polarizer (PGT-S1G). A series of the spectra were recorded using both the $x$- and $y$-polarized light, varying the angle between the surface normal of the film specimen and the direction of the light propagation −70, 0, +70°. Absorption intensities were corrected for the substrate and the host material absorptions to obtain the absorption intensity of porphyrin chromophores only. The calculations of orientation angles were based on the dependence between light absorption and orientation of transition moments. Generally, the probability of the transition due to photon absorption is proportional to $\cos^2\Theta$, where $\Theta$ represents the angle between the electric vector of the radiation and the orientation of transitional moment. Maximum absorption probability occurs when the vectors are parallel, and the probability approaches zero when the transitional moment is perpendicular to the electric vector of radiation. Dichroic ratios ($R$) were calculated for each measured wavelength from 350 to 700 nm using the formula

$$R(\lambda_i) = A_x(\lambda_i)/A_y(\lambda_i), \tag{1}$$

where $A_x$ and $A_y$ denote the absorption values measured using $x$- and $y$-polarized light, respectively. The dichroic ratio depends on the film tilt and the orientation of the transition moment with respect to the surface normal, according to [1,4,9,16]

$$R = \frac{2\sin^2\alpha - (3\sin^2\alpha - 1)\sin^2\gamma}{\sin^2\gamma}. \tag{2}$$

To calculate the angle $\gamma$, the data of $R(\lambda_i, \alpha_i)$ (where $\lambda_i =$ 350–700 nm and $\alpha_i = -70$, 0, and $+70°$) were applied. The calculation was performed on the basis of the functional relation among $R$, $\alpha$, and $\gamma$ in Eq. (2). Consequently, angles between the silicate surface and the transition moment of TMPyP molecule can be expressed by

$$\Theta = 90° - \gamma. \tag{3}$$

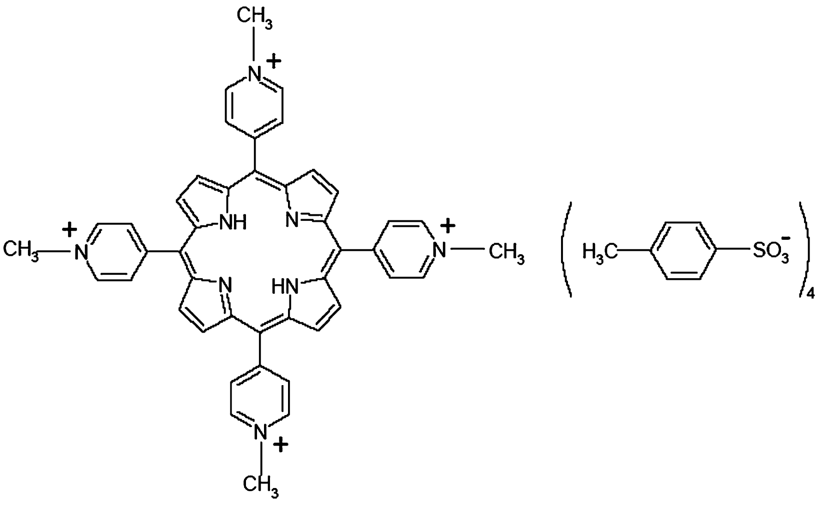
Fluorescence measurements were performed on a Shimadzu RF-5000 spectrofluorimeter. Spectra were recorded on excitation at 440, 460, and 520 nm at room temperature.

Linearly polarized infrared spectra were recorded on a FTIR Nicolet Magna 750 spectrometer in the middle infrared (IR) region (4000–400 $\text{cm}^{-1}$) using a ZnSe polarizer (Thermo Spectra-Tech). Principally the measurements were the same and the method is based on the same theory as in the case of linearly polarized UV–vis spectroscopy. Spectra were recorded for film tilt angles of 0, 40, and 50°. Due to a more complex character of the IR spectra, the dichroic measurements were only qualitatively evaluated to obtain information on the orientation of some functional groups of TMPyP, which could confirm the data of UV–vis-polarized spectroscopy.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1a shows the XRD patterns of sample FHT (dashed line) and diffraction patterns of FHT intercalated with TMPyP (solid line). Fluorohectorite has one of the largest values of particle diameter among expandable layered silicates, up to more than 10 μm [17], which results in sharp, well-resolved reflections in the XRD patterns. The position of $d_{001}$ peak in the case of FHT is 1.24 nm, which is referred to the sample with one intercalated layer of water molecules including respective inorganic cations [18]. After intercalation of TMPyP, we observed the changes in the position of the 001 band. The position changed from 1.24 to 1.90 nm. In Fig. 1b are plotted the XRD patterns for the film of KF before (dashed line) and after intercalation with TMPyP (solid line). The XRD patterns are very similar to the patterns of FHT and FHT_TMP (Fig. 1a). The



**Scheme 1.** Structural formula of 5,10,15,20-tetrakis($N$-methylpyridinium-4-yl)porphyrin (TMPyP), tetra-$p$-tosylate salt.

Download English Version:

https://daneshyari.com/en/article/611114

Download Persian Version:

https://daneshyari.com/article/611114

Daneshyari.com