



## Research paper

## Highly luminescent hybrid materials based on smectites with polyethylene glycol modified with rhodamine fluorophore

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## ABSTRACT

Highly luminescent anisotropic materials are promising for light harvesting systems, sensors, solid lasers and optical devices. To achieve this, polyethylene glycol (PEG) was derivatized with a reactive rhodamine B (RhB) fluorophore to produce a luminescent, water-soluble and positively-charged polymer (RhPEG) that can be intercalated between layers of smectites. An optimal degree of polymer derivatization was applied to avoid fluorescence quenching. The optical properties of RhPEG were similar to those of the RhB precursor. Colloids were prepared using RhPEG and the montmorillonite Kunipia (Mt) and the synthetic saponite Sumecton (Sap), with polymer/smectite mass ratios of 0.05–0.25, and were cast into thin solid films by a vacuum filtration deposition technique. The luminescent hybrid films exhibited a similar structure to those obtained by the intercalation of non-modified PEG. Optical properties depended considerably on the smectite type. The hybrid films made of Sap, the smectite with low charge density, negligibly induced the molecular aggregation of RhPEG and had high fluorescence quantum yields, similar to dilute solutions of RhB or RhPEG. On the other hand, the results of spectroscopic methods indicated molecular aggregation of RhPEG when intercalated between Mt layers leading to considerable fluorescence quenching, making this material unsuitable for the fabrication of photoactive optical films.

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## 1. Introduction

The property of smectites to exfoliate in aqueous colloids plays a significant role in their applications (Abend and Lagaly, 2000). In particular the small diameter of the particles (<50 nm) and low layer charge density are the most significant factors which contribute to the stabilization of smectite sols and gels even at high concentrations (Yamaguchi and Hoffmann, 1997). The surface of exfoliated particles is fully accessible for the adsorption of organic molecules or ions (Zhou et al., 2011). Colloidal dispersions based on fully exfoliated smectite particles are used for the synthesis of hybrid materials. Therefore, smectites are ideal precursors of organoclays and other hybrid materials. In particular optical hybrid materials, such as thin transparent films with perfect optical homogeneity and low light scattering can be prepared from stable colloidal precursors (Kawamata et al., 2010).

The properties of hybrid materials based on cationic dyes and smectites have been extensively studied (Bujdák, 2006; Liu and Zhang, 2007;

Zhou et al., 2011). The dye cations are almost irreversibly adsorbed onto the smectite particle surface (Rytwo et al., 1995), which is very important for the stability of hybrid materials. However, dye adsorption often leads to the formation of supramolecular assemblies called molecular aggregates (Bergmann and O'Konski, 1963; Bujdák, 2006). Dye aggregation causes significant changes in optical properties and leads to a reduction in dye photoactivity. Several strategies have been adopted to avoid molecular aggregation in the hybrid systems, including a suitable selection of the materials' components (Bujdák, 2006; Klika et al., 2009), modifications of the smectite surface (Bujdák et al., 2007; Salleres et al., 2008, 2009; Sasai et al., 2004), the optimization of synthesis routes and conditions (Bujdák and Iyi, 2012), or looking for new types of hybrid materials (Danko et al., 2013; Felheck et al., 2015; Fujii et al., 2008; Sas et al., 2015). A relatively new type of materials is photoactive hybrids with a covalent bonding between reactive dye molecules and clay mineral particles (Danko et al., 2013; Sas et al., 2015).

Besides the ion exchange and covalent bonding, there is one other way to achieve the irreversible adsorption of photoactive molecules: The adsorption of hydrophilic polymers on the smectite surface is promoted by the release of confined water molecules. H-bond formation between the released water molecules in a bulk phase, with the

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contribution of an entropic force effect, leads to a decrease in the free energy of the system. Materials based on clays and luminescent polymers have not been investigated much yet (Dong and Feng, 2005; Rullens et al., 2006). Luminescent polymers have found new applications in various industrial fields and research (Botiz et al., 2016). They are considered for various applications as new types of sensors in analytical chemistry, medicine and biological sciences (Ye et al., 2015) and as active components in photovoltaic applications (Griffini and Turri, 2016). Commercially available polymers with fluorescent moieties are expensive and there is a relatively limited selection of them (Alcantar et al., 2000).

Clay polymer nanocomposites have been extensively investigated over the last several decades. Materials based on clay minerals and hydrophilic polymers have been considered for various industrial applications, such as solid electrolytes, in medicine, cosmetics, drug delivery, etc. (De Villiers et al., 2011; Vaia et al., 1995; Zhou et al., 2011). Anchoring luminescent moieties onto the polymer chains would increase the functionality of these materials. For example, such materials could be developed and used in photonics applications (Olivero et al., 2012). Luminescent groups can be applied as molecular probes sensing structural changes in the composite material itself (Leone et al., 2013) or responding to the chemical environment (Dey et al., 2013; Zhou et al., 2011).

In this study, we designed a relatively simple and affordable route for modifying polyethylene glycol (PEG) with moieties of luminescent rhodamine (Rh) dye. The modification of the polymer was targeted to the  $-\text{CH}_2-\text{OH}$  end-groups of the PEG chains. A partial modification of PEG chains led to the luminescent material (RhPEG), which was soluble in water, and after its adsorption on the clay mineral surface, did not significantly destabilize aqueous dispersions of smectites. Similar to PEG (Zhao et al., 1989), RhPEG was irreversibly adsorbed onto the surface of smectite particles, thus forming stable hybrids with optical properties related to the Rh moieties present. The main objective of this work was to characterize hybrid materials based on RhPEG and two smectites, focusing mainly on their optical properties.

## 2. Materials and methods

### 2.1. Materials

Saponite Sumecton (Sap) (Utracki et al., 2007) and Kunipia montmorillonite (Mt) (Čeklovský et al., 2007) were both the products of Kunimine Industries (Japan); rhodamine B (RhB) was obtained from Sigma Aldrich (Germany) and PEG with an average molar mass of  $2000 \text{ g mol}^{-1}$  from Fluka. All these materials were used as received. Dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) from Mikrochem (Slovakia), dried over  $4 \text{ \AA}$  molecular sieves, and thionylchloride ( $\text{SOCl}_2$ ) (Sigma Aldrich) were distilled prior to use.

### 2.2. Polymer derivatization

In the first step, RhB carboxylic acid was activated by chlorination under reflux, using a mixture of dry  $\text{CH}_2\text{Cl}_2$  and freshly distilled  $\text{SOCl}_2$ , for 24 h under an argon atmosphere (Scheme 1). The formed acid chloride of RhB was used as a crude product after residual solvent and  $\text{SOCl}_2$  removal by vacuum distillation at room temperature. In the next step, the activated dye was reacted with the hydroxyl chain-end groups of PEG in dry  $\text{CH}_2\text{Cl}_2$  solvent in a 2.2:1 M ratio by reflux for 24 h (Scheme 1). After the reaction, the fluorescent polymer RhPEG was dialyzed to remove unreacted dye precursor using a Spectra/Por dialysis membrane with a molar mass cut off approximately  $1000 \text{ g mol}^{-1}$  (see Supplementary data, SD1a). A water/ethanol mixture was used for the dialysis, and after most of the unreacted RhB had been removed, the product was further washed in deionized water. The dialysis was carried out in several steps until the visible absorption of RhB had been detected in the supernatant using a UV-vis spectrometer. After the purification, RhPEG was lyophilized at 243 K and 1 Pa using a Labconco lyophilizer. The appearance of the product is shown in Supplementary data SD1b.

### 2.3. Preparation of colloids

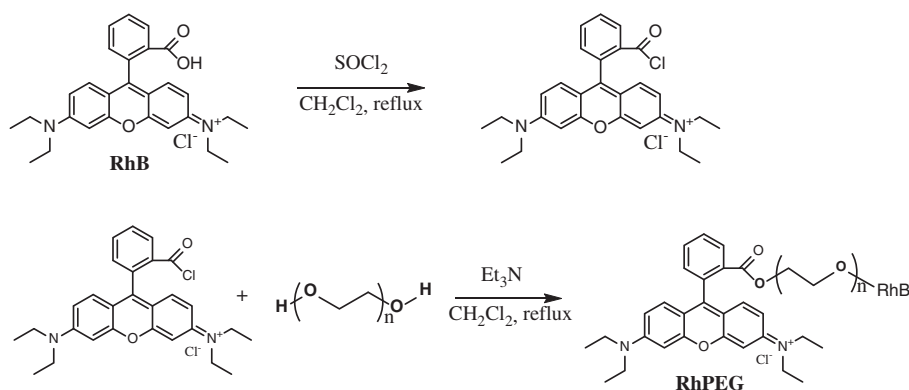
Colloidal dispersions were prepared by mixing an aqueous solution of RhPEG with the smectite colloid, prepared in deionized water one day prior to use. The final concentration of Sap or Mt smectites was  $0.1 \text{ g L}^{-1}$  with mass  $m_{\text{RhPEG}}/m_{\text{smectite}}$  ratios of 0.25; 0.20; 0.15; 0.10; and 0.05. Colloids with non-modified PEG of the same  $m_{\text{PEG}}/m_{\text{smectite}}$  ratios were also prepared for comparison. The colloidal dispersions were used as the precursors for the fabrication of thin films.

### 2.4. Preparation of hybrid films

Thin films were prepared from smectite colloidal dispersions using a vacuum filtration technique (Kawamata et al., 2010; Suzuki et al., 2008). The wet films retained on the surface of the filtration membranes ( $100 \text{ nm}$  pores) were transferred from the membrane onto the surface of quartz slides. The films exhibited good optical transparency and homogeneity (SD1c). Ten films, made of Sap or Mt with variable RhPEG/smectite ratios, were abbreviated as RhPEG<sub>x</sub>-Sap or RhPEG<sub>x</sub>-Mt, where  $x$  represents the  $m_{\text{RhPEG}}/m_{\text{smectite}}$  ratio ( $x = 0.05\text{--}0.25$ ). The hybrid films with non-modified PEG, PEG<sub>x</sub>-Sap and PEG<sub>x</sub>-Mt, were fabricated in the same way;  $x$  expresses the  $m_{\text{PEG}}/m_{\text{smectite}}$  ratios ( $x = 0.05\text{--}0.25$ ).

### 2.5. Methods

X-ray diffraction (XRD) was analysed using a Panalytical Empyrean in a  $2\theta$  range from  $2^\circ$  to  $15^\circ$ , using a step of  $0.02^\circ$ , counting time 2 s per step, and operating at 40 kV and 40 mA with  $\text{CuK}_\alpha$  radiation.



Scheme 1. Syntheses of RhB reactive dye precursor and fluorescent polymer RhPEG.

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