

Anisotropy of Fluorescence Dyes Intercalated into Nanostructured Interlayer Space of Clay Films.

F. López Arbeloa, V. Martínez, S. Salleres, J. Bañuelos, T. Arbeloa and I. López Arbeloa
 Physical Chemistry Department, University of the Basque Country, Bilbao, SPAIN
fernando.lopezarbeloa@ehu.es

The intercalation of fluorescence dyes into nanostructured host materials is fundamental in the design of new optical devices with interesting technological applications. Fluorescent dyes are normally used in photonics as active media of tunable dye laser. They are also successfully applied as molecular probes to study multitude of microheterogeneous systems, including biological systems, such as proteins, membranes, biosensors, etc. The fluorescence properties are generally dependent on the environmental characteristics and fluorescence techniques can provide information on the physicochemical properties of surrounding ambiances. Since fluorescence is a very rapid phenomenon, in the pico- and nano-second time-domains, these techniques can be applied to study the dynamics of very fast processes occurring in the excited states.

The adsorption of fluorescence dyes with a preferential orientation into nanostructured solid host materials can induce a macroscopic arrangement of fluorescence molecules with special interest in non-linear optics. In this contribution we show the anisotropy behaviour of rhodamine 6G (R6G) dye intercalated into laponite clay films with respect to the plane of the linearly-polarized light. This anisotropic photoresponse is a consequence of the preferential orientation of R6G molecules with respect to the plane of the films. Indeed, the absorption and fluorescence spectra of R6G with linearly polarized light can be used to evaluate the twisted angle of the long-molecular axis of R6G with respect to the layer of Lap clay [1].

Clay minerals are aluminosilicates with a lamellar structure formed by the condensation of tetrahedral (T) SiO_2 and octahedral (O) Al_2O_3 (dioctahedral) or MgO (trioctahedral) sheets. Part of the structural Si^{4+} , Al^{3+} or Mg^{2+} can be isomorphically substituted by cations with lower valence providing to the clay lamellas a net negative charge. This negative charge is compensated by inorganic cations (Na^+ , K^+ , Ca^{2+}) which are adsorbed at the external surface of the layers. These hydrated cations are interchangeable and induces the stacking of clay layers in parallel planes given rise to the tactoidal structure of clays with a interlayer distance around 1-2 nm (Figure 1(A)). This interlayer space is expandable and can accommodate a great variety of inorganic and organic cations by simple cation exchange mechanisms.

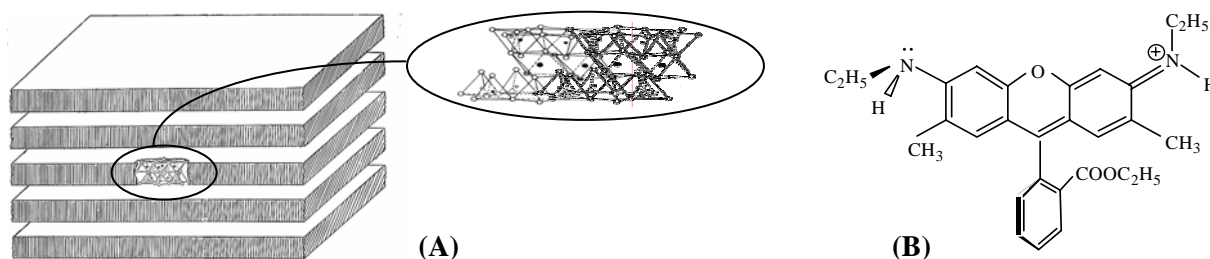


Figure 1. Tactoidal structure of clay minerals (A) and molecular structure of rhodamine 6G dye (B).

In this contribution we used the laponite (Lap) clay because it is characterized by its high chemical purity, its very low particle size (< 30 nm) and its very low iron content (iron is an efficient quencher for the fluorescence emission of many aromatic systems, including organic

dyes). Supported Lap films in glass substrate were obtained by the spin-coating technique. AFM images of these films reveal a correct topographic distribution of the Lap particles in the film. X-ray diffraction profiles suggest a parallel distribution of the Lap layers in the plane of the film. [2]

Rhodamine 6G (R6G, Figure 1 (B)) dye was chosen as fluorescence dye because probably this is the most-used laser dye. This fluorescent cation can be easily intercalated into the interlayer space of clays by simple cation exchange mechanism, for instance by immersion the Lap films into a dye solution. The loading of the dye can be controlled by the dye concentration in the immersion solution and the immersion time. The intercalation of R6G molecules into the interlayer space of Lap films was confirmed by XR diffraction technique.

The evolution of the absorption and fluorescence spectra of R6G in Lap films with the dye content suggest that R6G molecules can be adsorbed as different species such as monomeric (for low loadings) and as aggregates (moderated and high loadings). Both, non-fluorescent H-type and fluorescent J-type dimers and higher aggregates has been characterized in Lap films [3].

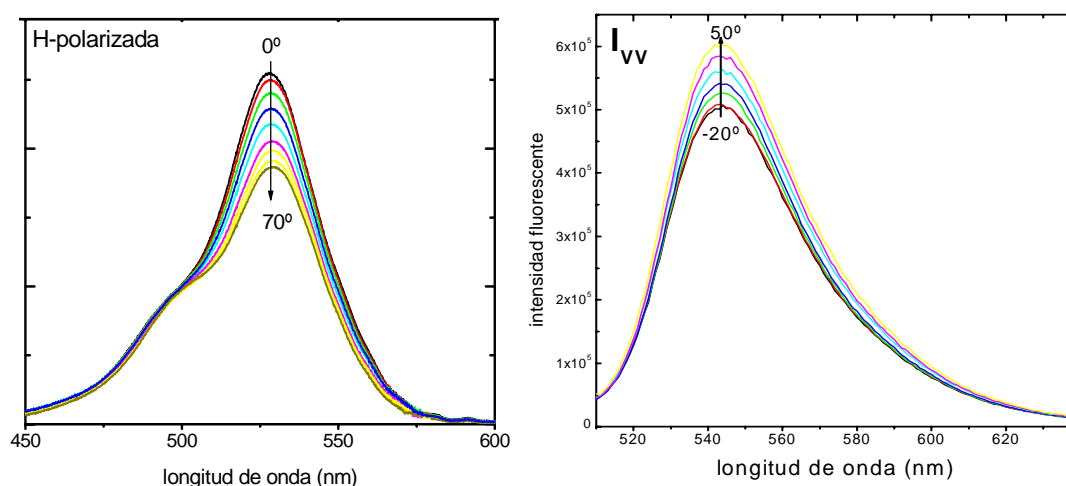


Figure 2: Evolution of the absorption (left) and fluorescence (right) spectra of a R6G/Lap film with the twisted angle for spectra recorded with linearly-polarized light

Figure 2 shows some representative evolution of the absorption and fluorescence spectra of R6G monomers adsorbed in Lap films with linearly-polarized light as a function of the twisted angle between the film and the incident beam. These anisotropic behaviours suggest a preferential orientation of R6G species adsorbed in the interlayer space of Lap films. From the linear relationship between the corresponding dichroic ratio and the twisted angle, the preferential angle of R6G species adsorbed on Lap film can be evaluated. Experimental results suggest that the R6G monomers are J-type aggregates are disposed with an orientation angle around 70° with respect to the normal to the Lap layers. H-type aggregates are disposed more to the perpendicular as the dye loading is increased.

Present results confirm that the adsorption of fluorescent dye into ordered clay layers is a good strategy to design new optical devices with an anisotropy response to the plane of linearly polarized light based in the incorporation of fluorescent dye into organized clay films.

[1] F. Lopez Arbeloa et al. *Chem. Mat.* **17** (2005), 4734 and **18** (2006) 1407

[2] V. Martinez et al. *Langmuir* **20** (2004), 4715

[3] V. Martinez et al. *J. Chem. Phys. B* **108** (2004), 20030 and **109** (2005), 7443