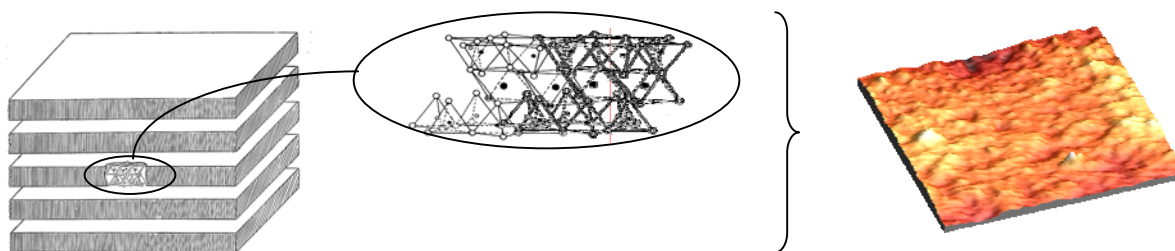


DESIGNS OF NEW OPTICAL SYSTEMS BASED IN THE INTERCALATION OF LASER DYES IN THE NANOSTRUCTURED INTERLAYER SPACE OF CLAY SOLID FILMS

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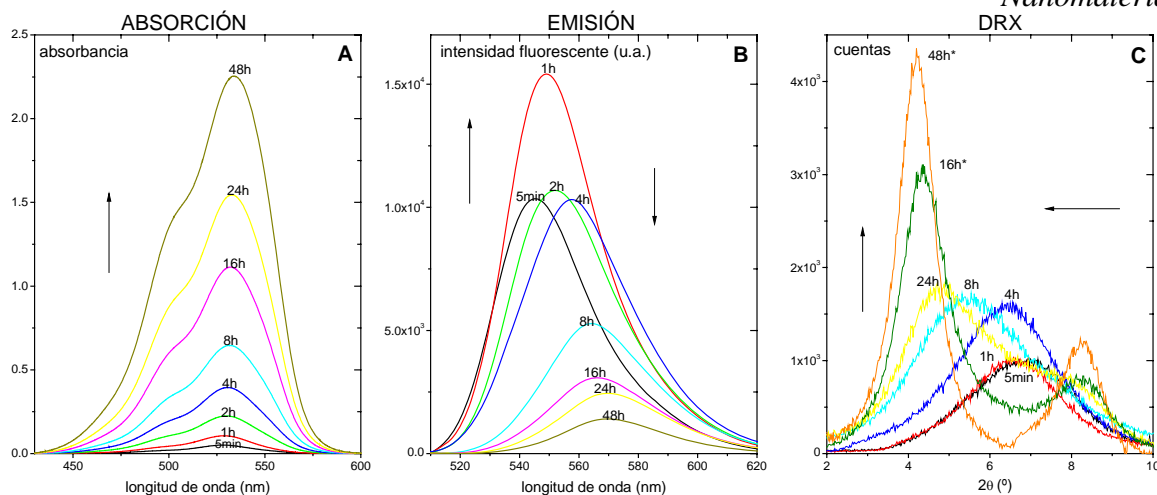
The synthesis of new multifunctional materials has been improved in the last years due to their potential applications in different scientific and technological areas such as Nanoscience and the Chemistry of the Intercalation. The development of new organic-inorganic hybrid materials tries to complement the optical, electronic or chemical properties of the guest organic molecules with the structural, mechanical and thermal characteristics of the host inorganic-type framework. The possibility to achieve oriented organic dye molecules in the 1-, 2- or 3-dimensional arrangement of organised host materials is fundamental on the design of new non-linear optical crystals and optoelectronic devices. These organised materials would present different photoresponse depending on the relative orientation of the material with respect to the incident light or on the orientation of the plane of linearly-polarized light.

In this contribution, we present the intercalation and orientation of laser-dye molecules (rhodamines) into the nanostructured interlayer space of clay particles [1]. Clay minerals are aluminosilicate materials with a lamellar structure. The layers are normally charged as a consequence of isomorphic substitutions of the structural cations by others of lower valence. These negative charges are compensated by interchangeable inorganic cations, inducing the stacking of clay layers, giving rise to the tactoidal structure of clays (Fig.1, left). The interlayer space of clay can swell to accommodate a great variety of organic compounds and the accessibility of the internal space depends on several factors such as the charge density, the type of the interchangeable cation and the solvation degree. Smectite-type clays, with moderated charge density, are the most recommended clay systems to adsorb organic cationic dyes. The interlayer distance in the tactoidal structure of smectite-type clays is in the nanometric-scale domain ($\approx 10 - 20 \text{ \AA}$).



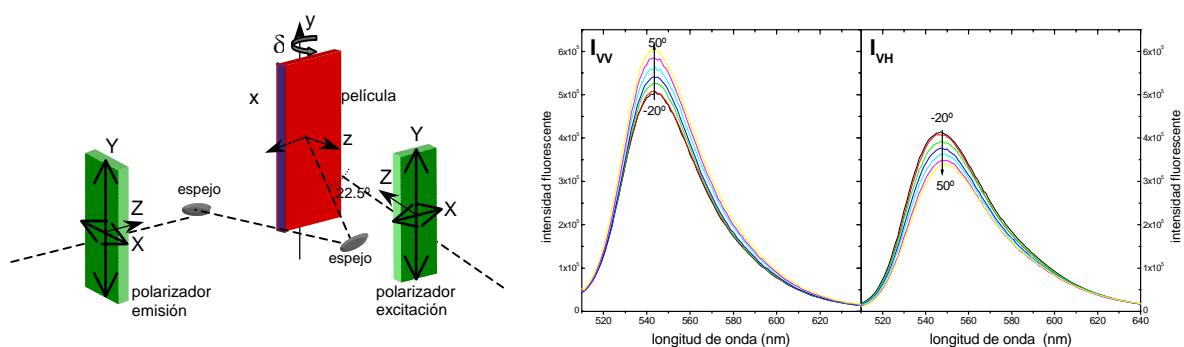
Supported thin films on glass substrates can be obtained by casting and by the spin-coating techniques. This last technique provided a macroscopic parallel arrangement of the clay layers into the substrate, as is revealed by AFM (Fig.1, right), with film thickness around 250 nm [1]. The encapsulation of the organic dye in the interlayer space of clay films was conducted by the immersion of the films in adequate liquid solutions of the dye. The intercalation can be checked by the X-ray diffraction technique (Fig.2, right) and the amount of intercalated dye (controlled by the immersion time and the dye concentration) can be evaluated by different techniques such as CHN analysis and different thermogravimetry techniques.

The photophysical properties of the dye adsorbed in the clay film can be characterized by the UV/Vis absorption and fluorescence spectroscopies. Increasing the dye concentration produces an enhancement of the color of the dye/clay films and a change in the shape of the absorption spectra (Fig.2, left). This change is ascribed to the aggregation of the dye. The



fluorescence intensity increases with the dye content for low loading samples to reach a maximal emission, but further increase in the dye concentration reduces the fluorescent emission (Fig.2, middle). Indeed, the fluorescence efficiency, analyzed as the fluorescence intensity over the absorbance of the sample at the excitation wavelength, diminishes when the dye content is increased due to the dye aggregation. H-type and J-type dimers and higher-aggregates of the dye are spectroscopically characterized in the interlayer space of the clay films from the evolution of the absorption and fluorescence spectra with the dye loading [2].

Finally, the orientation of dye species adsorbed in the clay films can be evaluated from the evolution of the absorption and fluorescence spectra with the twisted angle of the normal to the films with respect to the plane of the linearly-polarized light of the incident beam (in absorption) or the emission beam (in fluorescence). Fig.3 (left) shows a representative illustration for the experimental set-up used to record fluorescence polarization in the front-face mode where the excitation and emission-detection channels are oriented 22.5° . The anisotropy response of the dye/clay system is confirmed from the different evolution of the fluorescence spectra with the twisted angle of the sample for horizontal and vertical polarization (Fig. 3, right). The anisotropy response of dye/clay films is due to the preferential orientation of the dye in the interlayer space of the clay. The experimental results indicate that the monomer and J-type dimers are oriented around 62° with respect to the films normal and a more perpendicular orientation (around 28°) is obtained for H-type higher aggregates [3].



References:

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