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Journal of Photochemistry and Photobiology A: Chemistry 181 (2006) 44–49
Journal of Photochemistry and Photobiology A:Chemistry
www.elsevier.com/locate/jphotochem

New fluorescent polarization method to evaluate the orientation of adsorbed molecules in uniaxial 2D layered materials

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Received 21 September 2005; received in revised form 26 October 2005; accepted 26 October 2005
Available online 1 December 2005

Abstract

A new fluorescence polarization method is developed as a powerful tool to evaluate the preferential orientation of Rhodamine 6G (R6G) molecules adsorbed in the two-dimensional (2D) interlayer space of Laponite (Lap) clay films. The fluorescence anisotropy of a very low R6G loading film, around the 0.1% of the total cation exchange capacity (% CEC) of Lap, reveals that the dye is adsorbed as monomeric units with a preferential orientation angle of 62° with respect to the normal to the clay layers. This tilted angle agrees with that previously obtained by absorption spectroscopy with linearly polarized light [V. Martínez Martínez, F. López Arbeloa, J. Bañuelos Prieto, I. López Arbeloa, Chem. Mater. 17 (2005) 4134–4141], justifying the validity of the present emission technique. The fluorescent method can be applied to evaluate the orientation of any fluorescent molecules preferentially adsorbed along the normal of the plane of any rigid 2D host arrays.

Keywords: Dye adsorption; Clay thin; Anisotropy; Fluorescent polarization

1. Introduction

The design and study of ordered systems are of great interest from scientific and practical points of view. The synthesis of functional organized assemblies, e.g., intercalation of photofunctional organic molecules into rigid inorganic frameworks, can induce a preferential orientation of the photoactive compounds in macroscopic-scale domain. Soft and rigid surroundings with one-, two- and three-dimensional architectures are now available. Thus, supported films of layered materials can provide high-ordered two-dimensional (2D) macroscopic arrangements for the guest molecules [2,3]. The anisotropic nature of the final host–guest hybrid materials can present potential applications in optical and optoelectronic devices [4].

Several techniques such as optical dichroism [5,6], absorption and fluorescence with polarized light and second-order generation [7] methods can be applied to determine the anisotropy of adsorbed molecules in ordered host materials. For instance, the absorption spectroscopy with linearly polarized light has been extensively applied to evaluate the preferential orientation of dye molecules adsorbed in clay films [8–12].

Rhodamine 6G (R6G, Fig. 1 (top)) laser dye has been successfully intercalated in solid thin films of Laponite (Lap) clay [3]. Lap is a smectite-type clay mineral with a layered structure due to the condensation of an octahedral (O) MgO sheet between two tetrahedral (T) SiO_2 sheets. Some of the Mg^{2+} cations are substituted by Li^+ giving rise to a net negative charge of the TOT layers, which are compensated by inorganic exchangeable cations localized in the layer surface. R6G dye was chosen because it is probably the most-used dye in tunable lasers and the design of new environments improving their optical, photophysical and lasing properties is of great technological interest. On the other hand, the smectite-type clays are especially attractive mineral materials due to their high area/weight ratio and cationic exchange capacity able to accommodate many ionic and polar organic compounds in the interlayer space. Moreover, Lap films are transparent to the Vis electromagnetic radiation and provide ideal 2D rigid environments for cationic dye molecules [3].

The adsorption of R6G molecules in the interlayer space of Lap films was performed by immersing the Lap films into different R6G solutions and the dye loading was controlled by the dye concentration (from 10^{-6} to 10^{-3} M) and the immersion time (from 5 min to 2 days). The intercalation of the dye molecules

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doi:10.1016/j.jphotochem.2005.10.031

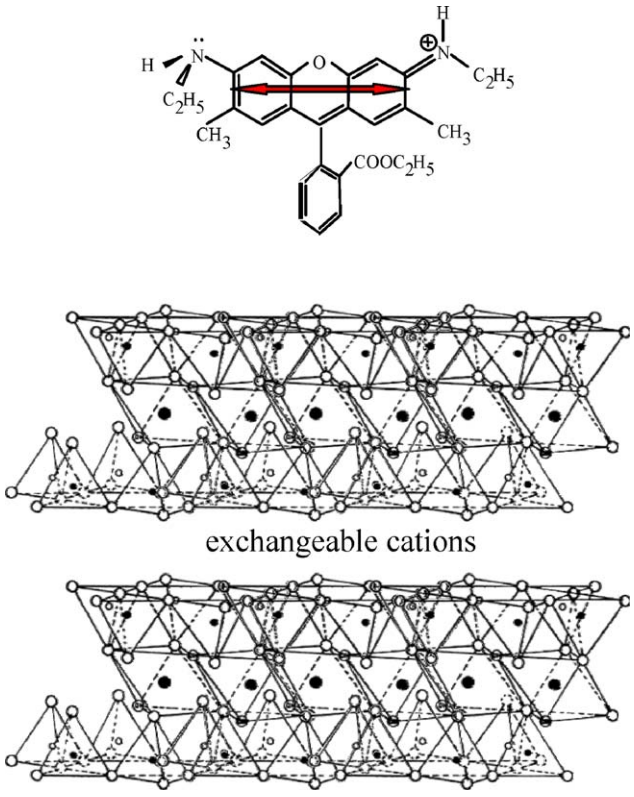

Fig. 1. Molecular structure of R6G (top) and layered structure of Lap clay minerals (bottom).

in the interlayer space of Lap films was previously checked by X-ray diffraction technique [3]. The increase in the dye content produces the dye aggregation and several dimers and higher aggregates of R6G in Lap films were characterized by absorption and fluorescence spectroscopy [13,14]. The preferential orientation of monomer, dimers and higher-order aggregates of R6G was determined by absorption spectroscopy with linearly polarized light [1].

In the present paper a new method is developed in order to evaluate the preferential orientation of immobile fluorescent molecules adsorbed in a rigid host surface. The method is based on the evolution of the fluorescence dichroic ratio with the twisted angle of the sample with respect to the incident beam. In order to check the validity of the present fluorescence method, it is applied to the adsorption of R6G monomers encapsulated in the interlayer space of supported thin films of Lap clay [1,3]. This preferential orientation was previously determined by absorption polarization, with a tilted angle between the long molecular axis of the dye and the normal to the clay layer of 62° [1].

The new method is based on the different response of the fluorescence spectrum of ordered systems to the horizontal and the vertical directions of the emission polarizer for different orientations of the film with respect to the emission beam. The developed method is not only applicable for ordered dye/clay films, but it can also be extended to evaluate the preferential orientation of any fluorophore adsorbed in macroscopically organized 2D materials.

2. Experimental

Rhodamine 6G (Laser Grade) was supplied Kodak and was used as received. Laponite B was provided by Lapporte Industries and did not require additional treatment, since this synthetic clay is characterized by its high purity, low particle size and in sodium form.

Ordered Lap films supported on glass substrates were prepared by the spin coating technique [3]. R6G molecules were incorporated to the interlayer space by immersing the film in a liquid solution of the dye (further details of the sample preparation are described elsewhere [3]). The final dye loading, controlled by the immersion time (5 min) and the dye concentration (10^{-5} M) in the solution, was fitted at around 0.1% of the total cation exchange capacity of the clay (0.1% CEC). For this loading, the R6G molecules are adsorbed in the Lap film as monomeric units [13,14].

Fluorescence spectra were recorded in a SPEX spectrofluorimeter (model Fluorolog 3–22), equipped with automated Glan–Thompson polarizers in both the excitation and the emission beams. The fluorescent spectrum of the film was registered after excitation at 495 nm by the front-face configuration, where the fluorescence emission was collected along the Z'-axis at 22.5° with respect to the excitation beam in the Z-axis (see Fig. 2). The fluorescence spectra were scanned in the 510–640 nm range, every 2 nm, at an integration time of 2 s, with excitation and emission slits of 8 and 2 nm, respectively.

The orientation of the film with respect to the excitation beam was changed by rotating the solid-sample holder around its vertical y-axis. Indeed, the angle between the normal to the film and the excitation axis (defined as the δ angle in Fig. 2) was scanned from −20 to 50°. The instrumental response to the linearly polarized light has been corrected by recording the fluorescent signal of an isotropic system at identical experimental conditions. In the present work, a 10^{-5} M solution of R6G in ethanol in a 1mm pathway cell was used as isotropic system.

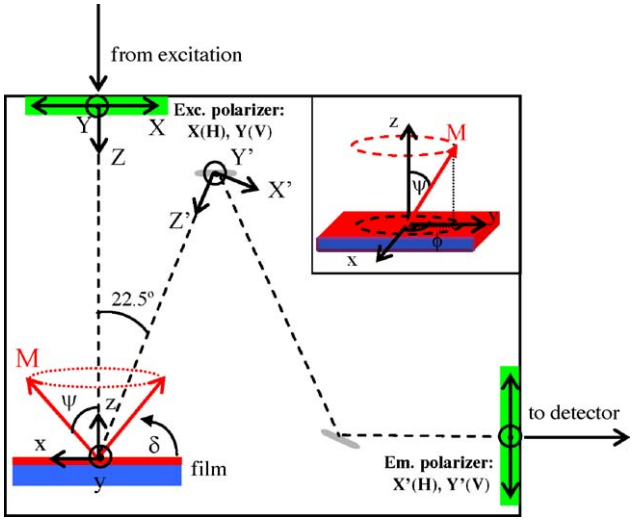

Fig. 2. Top-view of the experimental set-up used to record fluorescence spectra with polarized light in the front-face configuration of a Fluorolog 3–22 fluorimeter.

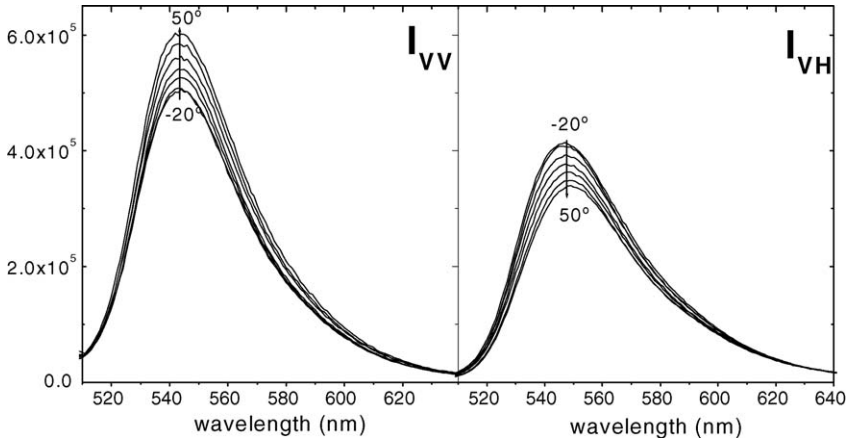

Fig. 3. Corrected-polarized fluorescence spectra of the 0.1% CEC R6G/Lap film for different twisted δ angles of the sample with respect to excitation beam. The emission polarizer was horizontally (I_{VH}, right) and vertically (I_{VV}, left) oriented with respect to the vertically polarized excitation light.

3. Results and discussion

Fluorescence spectra with polarized light were recorded for the emission polarizer in the vertical position, I_{VV} (emission Y'-axis, Fig. 2) and in the horizontal direction, I_{VH} (X'-axis), keeping constant the excitation polarizer in vertical orientation (excitation along the Y-axis). Fig. 3 shows the evolution of the fluorescence spectra of the R6G/Lap film with the emission polarizer in vertical (left) and horizontal (right) orientations, respectively, as a function of the twisted δ angle of the sample. These spectra were corrected for the response of the instrumental components to the plane of the polarized light by considering the changes obtained in the recorded fluorescence spectra of an isotropic system (a liquid solution of R6G, see Section 2) with the emission polarizer oriented in the horizontal and the vertical directions (see later in the text). As is revealed from Fig. 3, the fluorescence intensity of R6G monomer gradually increases/decreases by increasing the twisted angle δ when the emission polarizer is vertically/horizontally oriented. These opposite evolutions suggest a fluorescent anisotropic behaviour of the R6G/Lap film, ascribed to the preferential orientation of the R6G monomers adsorbed on the Lap layers. The angle of this orientation can be evaluated from the evolution of the polarized fluorescence intensity with the twisted angle of the sample, as is now mathematically developed on the basis of general concept of fluorescence polarization [15–17].

Under the conditions used in the present work (vertically Y-polarized excitation and vertically Y'- and horizontally X'-polarized emission), the fluorescence intensities for vertical and horizontal emission polarizers are given by:

$$I_{VH} \propto I_{abs}(Y) k_{flu}(X') \quad (1)$$

$$I_{VV} \propto I_{abs}(Y) k_{flu}(Y') \quad (2)$$

where $I_{abs}(Y)$ is the absorption intensity of the films for the vertically polarization at the excitation wavelength and $k_{flu}(X')$ and $k_{flu}(Y')$ are the radiative rate constants of the horizontally and vertically polarized emission light, respectively. The fluorescence dichroic ratio, defined as the ratio between both detected emissions ($D_{H,V} = I_{VH}/I_{VV}$), can be simplified to $k_{flu}(X')/k_{flu}(Y')$ for a constant excitation process.

On the other hand, k_{flu} is proportional to the square of the transition dipole moment ($\vec{M}$), and for a given polarization orientation, it is proportional to the square of the projection of $\vec{M}$ in that direction. Therefore, $k_{flu}(X')$ and $k_{flu}(Y')$ are proportional to $M^2_{X'}$ and $M^2_{Y'}$, respectively. In order to obtain an expression relating the dichoic ratio and the emission transition moments of the fluorophores, it is necessary to align the x-, y- and z-axes of the sample with the X', Y' and Z'-axes of the emission coordinates.

$$k_{flu}(X') \propto M^2_{X'} = S_H[M_x \cos(xX') + M_y \cos(yX') + M_z \cos(zX')]^2 \quad (3)$$

$$k_{flu}(Y') \propto M^2_{Y'} = S_V[M_x \cos(xY') + M_Y \cos(yY') + M_Z \cos(zY')]^2 \quad (4)$$

where S_H and S_V are the sensitivity factors of the emission channel for the horizontal and vertical polarization components, respectively. These factors can be corrected by recording the fluorescence response to both horizontal and vertical emission polarizers of an isotropic system. Indeed, the fluorescence spectra shown in Fig. 3 have been corrected for the instrumental response to the emission H- and V-polarized light of a 10^{-5} M solution of R6G in ethanol recording in identical conditions (front-face configuration in a 1 mm pathway cell and for all twisting δ angle from -20 up to 50°).

The angles between (x, y, z) and (X', Y', Z')-axes are related with the α, β and γ Euler angles (Fig. 4) [15]; γ is the rotation angle around z-axis to translate the x-axis into the XY-plane; β is the turning angle around the y-axis of the sample to bring z-axis into Z-orientation; and α is the rotational angle around the new z-axis to make coincident x- with X-axis and y- with Y-axis.

Taking as positive angles the counter-clock-wise rotation, the Euler angles for the present experimental set-up (see Fig. 2) are: $\alpha = \gamma = 0^\circ$ and $\beta = 180 - (22.5 + \delta)^\circ$, where 22.5° is the angle between the excitation and the emission beams in the front-face configuration of a Fluorolog 3–22 SPEX fluorimeter. The value

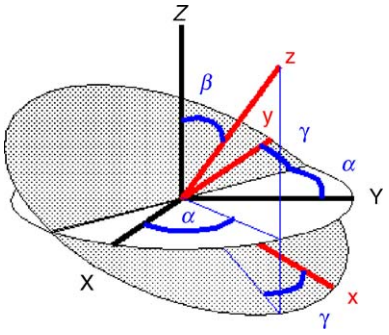

Fig. 4. Euler angles converting the *XYZ*-coordinates in the *xyz*-axes.

of the direction cosines are related to the Euler angles by means of [15]:

$$\cos(xX') = \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma = -\cos(22.5+\delta) \quad (5)$$

$$\cos(yX') = -\sin\alpha\cos\gamma - \cos\alpha\cos\beta\sin\gamma = 0 \quad (6)$$

$$\cos(zX') = \cos\alpha\sin\beta = \sin(22.5+\delta) \quad (7)$$

$$\cos(xY') = \cos\alpha\sin\gamma + \sin\alpha\cos\beta\cos\gamma = 0 \quad (8)$$

$$\cos(yY') = \cos\alpha\cos\gamma - \sin\alpha\cos\beta\sin\gamma = 0 \quad (9)$$

$$\cos(zY') = \sin\alpha\sin\beta = 0 \quad (10)$$

On the other hand, the x, y and z components of M are related to the polar ψ and ϕ angles by:

$$M_x = M\sin\psi\cos\phi \quad (11)$$

$$M_y = M\sin\psi\sin\phi \quad (12)$$

$$M_z = M\cos\psi \quad (13)$$

(see inset Fig. 2). ψ defines the angle between the transition moment $\vec{M}$ and the normal to the film (z) and ϕ is the angle between the projection of $\vec{M}$ into the xy-plane (M_{xy}) and the x-axis. Applying Eqs. (5)–(13) to Eqs. (3) and (4):

$$k_{\text{flu}}(X') = S_{\text{V}}M^2[\sin\psi\cos\phi\cos(22.5+\delta) + \cos\psi\sin(22.5+\delta)]^2 \quad (14)$$

$$k_{\text{flu}}(Y') = S_{\text{H}}M^2[\sin\psi\sin\phi]^2 \quad (15)$$

In the present sample (a dye adsorbed in clay layers) the adsorbed fluorophores only have a preferential orientation with respect to the z-axis of the film, whereas they do not present an anisotropic distribution in the xy-plane of the film (all the orientations of $\vec{M}$ in the xy-plane are equally probably) [1]. Then, the ψ angle actually represents the preferential orientation of the fluorescent molecules adsorbed into the film, while the ϕ angle can take any value between 0° and 360°. So, the average values in all those functions which depend on the ϕ parameter have to be considered. For instance,

$$\overline{\sin\phi} = \overline{\cos\phi} = \int_0^{360}\cos\phi\,\mathrm{d}\phi = 0 \quad (16)$$

$$\overline{\sin^2\phi} = \overline{\cos^2\phi} = \int_0^{360}\cos^2\phi\,\mathrm{d}\phi = \frac{1}{2} \quad (17)$$

Applying Eqs. (16) and (17) to Eqs. (14) and (15):

$$k_{\text{flu}}(X') = S_{\text{H}}M^2[\tfrac{1}{2}\sin^2\psi\cos^2(22.5+\delta) + \cos^2\psi\sin^2(22.5+\delta)] \quad (18)$$

$$k_{\text{flu}}(Y') = S_{\text{V}}M^2[\tfrac{1}{2}\sin^2\psi] \quad (19)$$

So, the fluorescent dichroic ratio becomes:

$$D_{\text{H,V}} = \frac{I_{\text{VH}}}{I_{\text{VV}}} = \frac{S_{\text{H}}}{S_{\text{V}}} \frac{\left[\frac{1}{2}M^2\sin^2\psi\cos^2(22.5+\delta) + M^2\cos^2\psi\sin^2(22.5+\delta)\right]}{\frac{1}{2}M^2\sin^2\psi} \quad (20)$$

The first term is related to the different efficiencies of the instrumentation for the detection of H- and V-polarizations. To correct these effects, the instrumental response to X'- and Y'-polarizations of an isotropic system has to be recorded (e.g., a dye in a liquid solvent). The dichroic ratio for the isotropic system is given by: $(D_{\text{H,V}})^{\text{iso}} = (I_{\text{VH}}/I_{\text{VV}})^{\text{iso}} = S_{\text{H}}/S_{\text{V}}$. The inverse of the value is commonly known as the G factor ($S_{\text{V}}/S_{\text{H}}$). The isotropic factor must be recorded for all the orientations of the sample compartment (δ angle from −20 to 50°) in order to correct also the variation of the instrumental excitation and fluorescence signals with the sample orientation.

Finally, the corrected dichroic ratio of the sample is related to the preferential orientation of the fluorophore ψ angle by means of:

$$(D_{\text{H,V}})^{\text{cor}} = \frac{I_{\text{VH}}}{I_{\text{VV}}}\left(\frac{I_{\text{VV}}}{I_{\text{VH}}}\right)^{\text{iso}} = \frac{I_{\text{VH}}}{I_{\text{VV}}} \times G = 2\cot^2\psi + (1-2\cot^2\psi)\cos^2(22.5+\delta) \quad (21)$$

From the linear relationship between $(D_{\text{H,V}})^{\text{cor}}$ and $\cos^2(22.5+\delta)$, the tilted ψ angle can be evaluated from both the slope and the intercept ordinate. The isotropic G factor in Eq. (21) not only corrects the instrument response to the H- and V-polarized light, but also takes into account the changes in the fluorescence intensity caused by the variation of the sample position (optical pathways and reflections) with the δ angle.

Eq. (21) is no longer valid if some depolarization phenomena can occur during the lifetime of the fluorescent state. The most important depolarization processes affecting Eq. (21) are [15–17]:

(i) non-parallel absorption and emission transition moments;
(ii) rotational motions of the fluorescent molecules during the excite-state lifetime;
(iii) excitation energy migration and/or transfer to a second molecule with its transition moment oriented in a different direction;
(iv) other trivial causes of depolarization such as light scattering, reabsorption and reemission phenomena . . ..

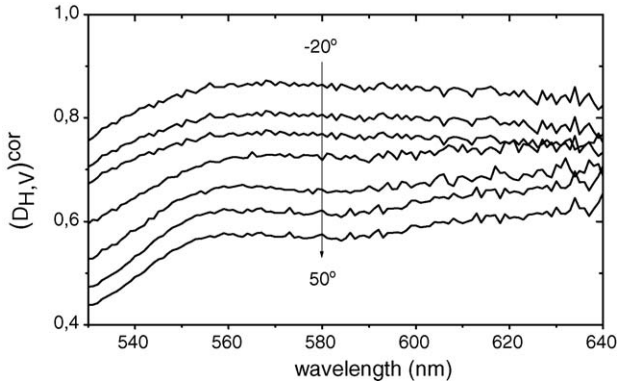

Fig. 5. Corrected fluorescence dichroic ratios of the 0.1% CEC R6G/Lap film as a function of the emission wavelength for different twisted δ angles.

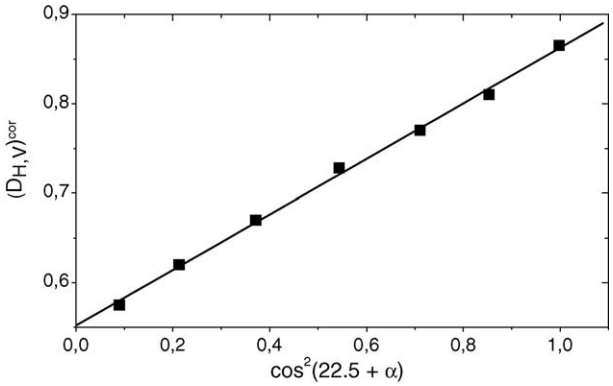

Fig. 6. Linear relationship between the fluorescence dichroic ratio and the twisted δ angle for the 0.1% CEC R6G/Lap film.

However, none of these phenomena are present in the 0.1% CEC R6G/Lap film:

- The main absorption band and the fluorescent transition of rhodamine dyes involve the S_0 and S_1 singlet states, both radiative processes are of identical nature and consequently they are parallel each other. Quantum mechanic calculations suggest that the transition dipole moment for the $S_0 - S_1$ spectroscopic transition is oriented along the long molecular axis, as is shown in the molecular structure of Fig. 1.
- On the other hand, time-resolved fluorescence decay curves of R6G/Lap films [14] reveals the absence of any reorientation of the adsorbed dye molecules during their fluorescence lifetime. Indeed, identical decay curves were previously recorded for the 0.1% CEC R6G/Lap films with the emission polarizer horizontally, vertically and in the magic-angle directions for vertically polarized excitation pulses.
- Energy transfer and reabsorption/reemission phenomena can be ruled out in the present 0.1% CEC film, because bimolecular processes for this very low dye content sample should be insignificant.
- Finally, the influence of the light scattering should be more important at shorter emission wavelengths (close to the excitation wavelength). This effect should be more important for the emission polarizer with the same orientation to that used in the excitation beam (e.g., the emission V-polarizer for V-polarized excitation light used in the present case) than for the crossed excitation and emission polarizers configuration (the H-emission component for a V-excitation component). This effect can, in some extent, be corrected by the isotropic G factor used to correct the instrumental response to the polarized light.

The fluorescence dichroic ratio for the R6G monomer adsorbed in Lap films is determined from the recorded fluorescence spectra of the 0.1% CEC R6G/Lap films shown in Fig. 3. The evolution of the dichroic ratio with the emission wavelength for different twisted angles of the sample is illustrated in Fig. 5. These results suggest that the $(D_{V,H})^{cor}$ value is nearly independent of the emission wavelength, confirming the presence of only one fluorescent R6G species in the Lap film. Indeed, and as was previously concluded [13,14], R6G molecules are adsorbed as individual monomeric units for this very low R6G/Lap films loading (0.1% CEC) used in this work. The progressive loss in the $(D_{V,H})^{cor}$ value in the short wavelengths region could be ascribed to non-totally correction of the scattering of the excitation light. Indeed, the light scattering of the isotropic system (a liquid solution in a polished quartz cell) is much lower than that observed for the Lap film. Consequently, the $(D_{V,H})^{cor}$ value obtained in the short-wavelength region should be affect by the light scattering.

According to Eq. (21), the fluorescence dichroic ratio linearly correlates with the twisting angle δ of the sample by means of the $\cos^2(\delta + 22.5)$ function for a given emission wavelength. Such a linear relationship is illustrated Fig. 6 for a fluorescence wavelength close to the emission peak. The good linear relationship observed in this representation, with a correlation coefficient $r = 0.9988$, suggests the validity of the above assumptions related with the absence of any depolarization phenomena during the lifetime of the dye in this very low loading R6G/Lap films and the powerfully application of the fluorescence polarization method to evaluate the orientation of R6G molecules adsorbed in Lap films. Similar plots are observed for other emission wavelengths.

From the intercept and the slope of the $(D_{V,H})^{cor}$ versus $\cos^2(\delta + 22.5)$ obtained in Fig. 6, the orientation ψ angle of the transition moment of R6G monomer with respect to the normal to the Lap layers can be evaluated. The obtained values, 62° from the intercept and 61° from the slope, agree with the orientation angle previously reported by Vis-absorption spectroscopy with linearly polarized light for the same R6G/Lap film ($\psi = 62°$) [1], confirming the validity of the new fluorescence polarization method developed in the present work to evaluate the preferential orientation of fluorescent molecular probes adsorbed in rigid 2D layered materials.

Fluorescence techniques present certain advantages over absorption spectroscopy:

- Higher sensitivity, since the emission techniques record absolute intensities versus absorption spectroscopy, where the

absorption intensity is always referred to a background signal.

- Higher selectivity, because the presence of two monochromators allows the selection of two working wavelengths: the excitation and the emission wavelengths. In this sense, two absorbing species with similar absorption properties could be easily distinguished by fluorescence spectroscopies by adequate selection of the excitation and emission wavelengths.
- Fluorescence techniques provide two polarizers increasing the possibility to study the anisotropic systems. For instance, anisotropy can be studies by polarizing the excitation beam, or by polarizing the detection channel, or more usually a combination of both polarizers.

4. Conclusions

A new experimental method based on the fluorescence with linear polarized light is developed in this work to evaluate the preferential orientation of Rhodamine 6G molecules adsorbed in the interlayer space of a macroscopically ordered Laponite film. The fluorescence polarization reveals that the monomers of the dye are oriented 62° with respect to the normal of the film. This value agrees with that previously reported by absorption with polarized light [1], confirming the validity of the fluorescence method. A similar attitude can also be used to evaluate the preferential orientation of fluorescent molecular probes incorporated in uniaxial 2D-ordered host materials. The method is suitable for rigid diluted systems, where the diffusional rotations of the adsorbed fluorophores during its excited-state lifetime, the excitation energy transfer or migration and the reabsorption/reemission processes are restricted and cannot cause any fluorescence depolarization phenomena.

Acknowledgements

The University of the Basque Country is thanked for financial support (9/UPV00039.310-15264/2003). V.M.M. thanks the MECD Spanish Minister for a research grant.

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