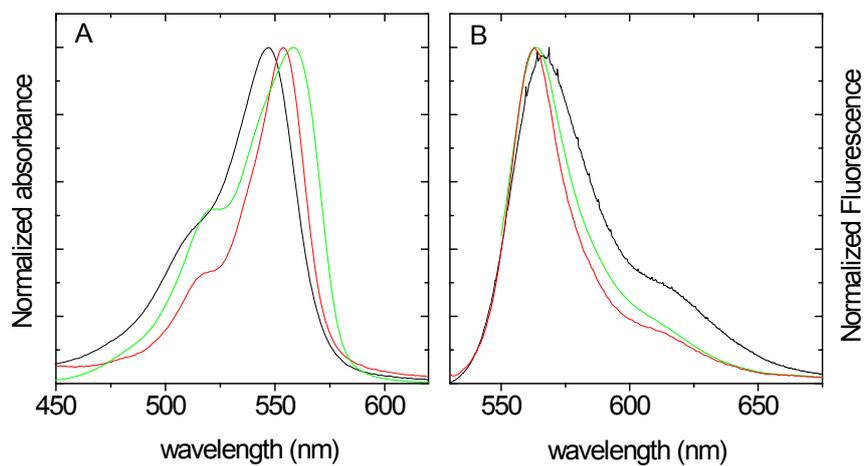


## Supporting Information for:

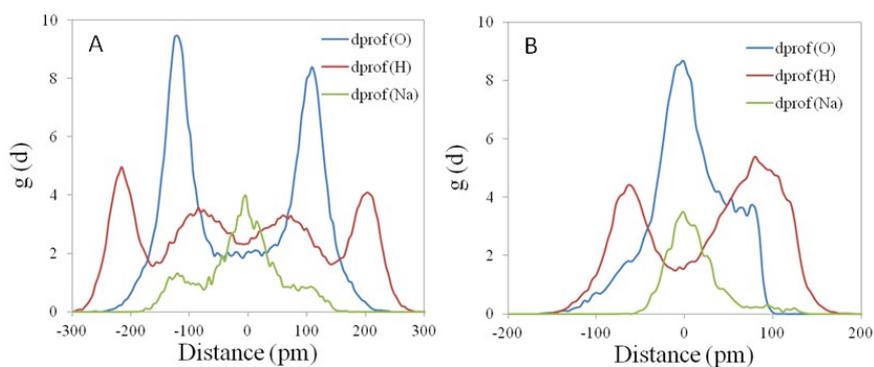
# Strategies for Modulation the luminescent properties of Pyronin Y- clay Films: Experimental and Theoretical Study

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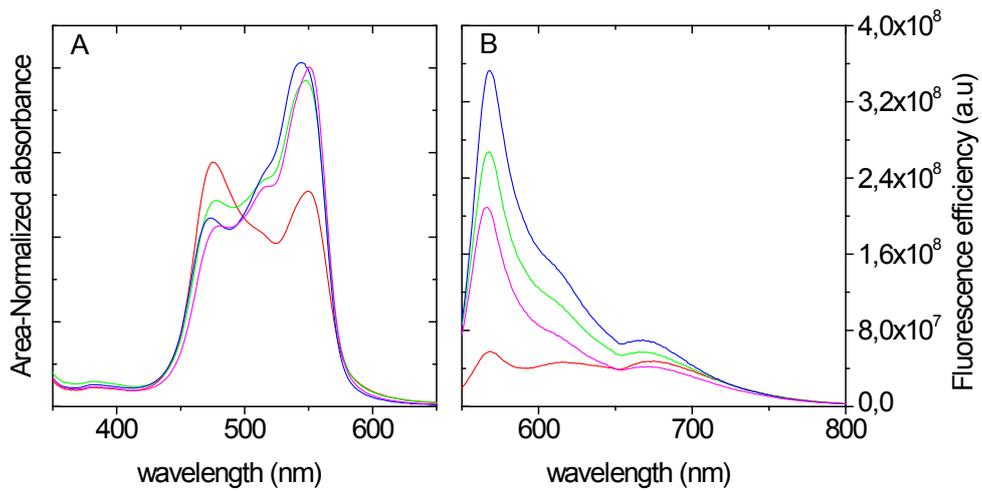
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**Figure S1.** (A) Absorbance spectra and (B) Fluorescence spectra of PY in different media: water solution (black), diluted PY/Sap film of 0.9% CEC (red) and diluted PY/Lap film of 0.5% CEC (green).



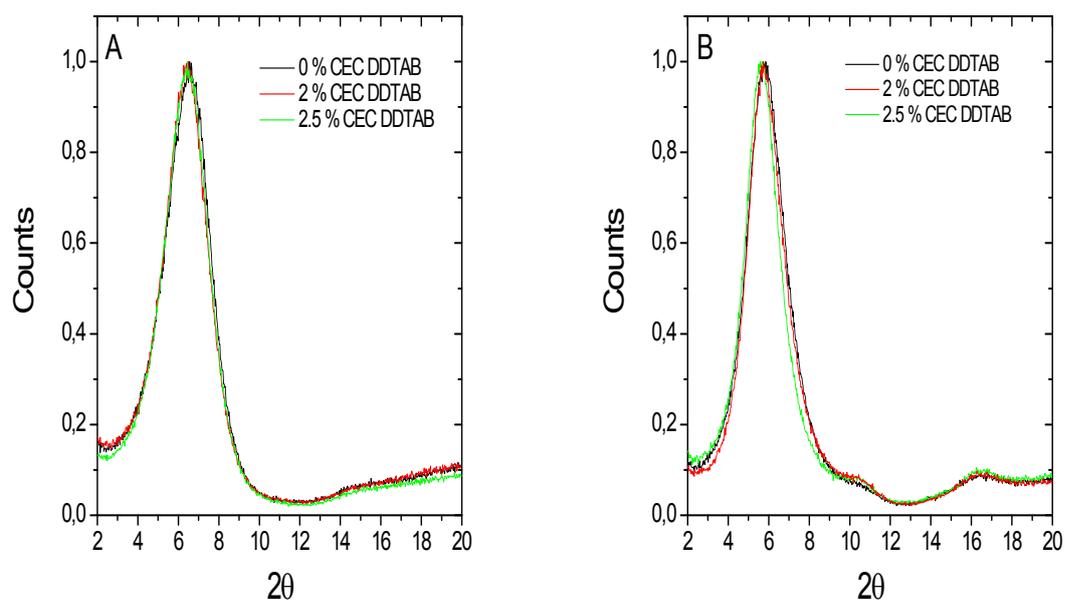
**Figure S2.** Density profile of O atoms (blue), H atoms (red) and Na cations (green) of (A) PY/Lap films and (B) PY/Sap films.



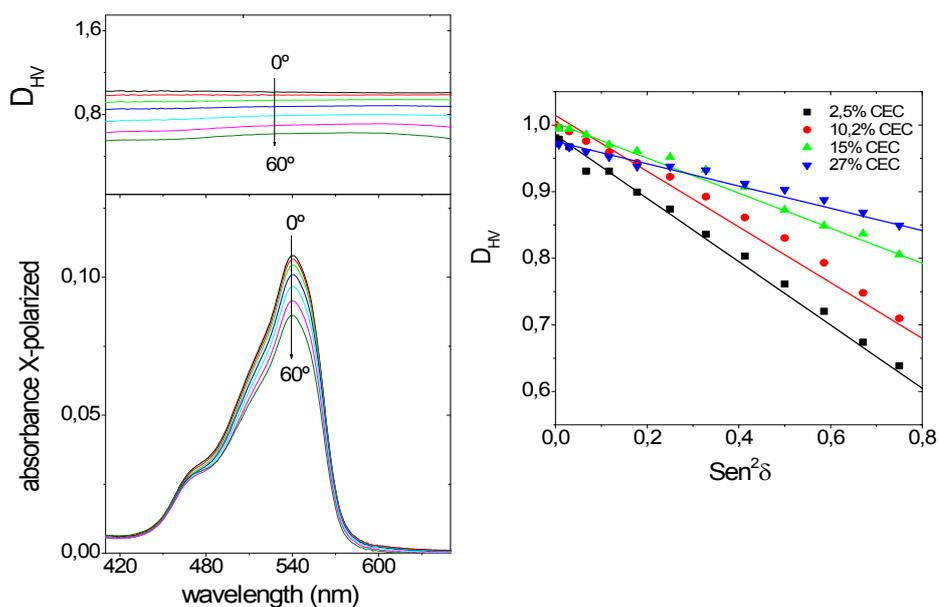
**Figure S3.** (A) Absorbance spectra and (B) fluorescence efficiency spectra of Lap films with PY dye and Surfactant intercalating simultaneously varying the relative dye:surfactant concentration: 1:0 (blue), 1:1 (red), 5:1 (green) and 15:1 (pink).

**Table S1.** XRD results for Lap film with different surfactant and dye loading;  $t_{imm}$  DDTAB and  $t_{imm}$  PY are the immersion time of the pure Lap film into  $10^{-6}$  M 50/50 v/v water/EtOH DDTAB and  $10^{-5}$  M 50/50 v/v water/EtOH PY solutions, respectively.

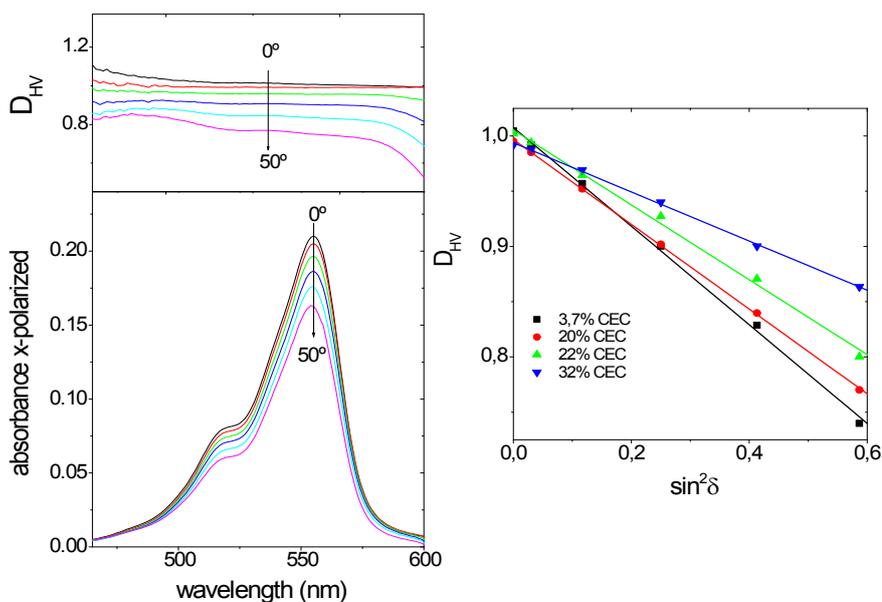
$t_{imm}$ DDTAB	%CEC DDTAB	$t_{imm}$ PY	%CEC PY	$2\theta$	d001
0	0	0.75	2.5	6.6	13.40
2h	2	0.75	2.4	6.5	13.60
6h	2.5	0.75	2.4	6.4	13.80
0	0	8	10.2	5.8	15.24
2h	2	8	9.3	5.7	15.50
6h	2.5	8	9.3	5.7	15.50



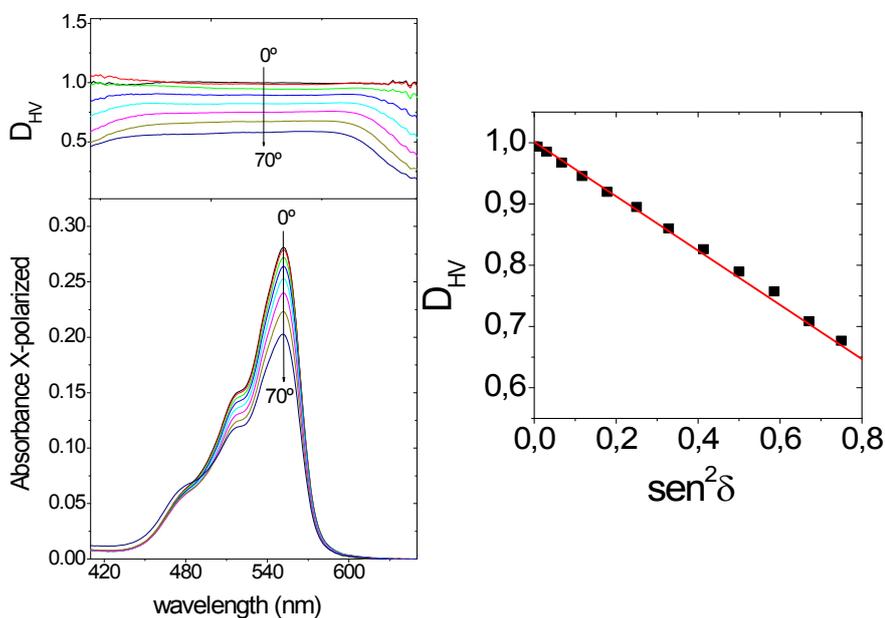
**Figure S4.** Normalized X-ray diffraction 001 peaks of Lap films for a A) PY loading of a 2.5% CEC and B) PY loading of 10.2 % CEC



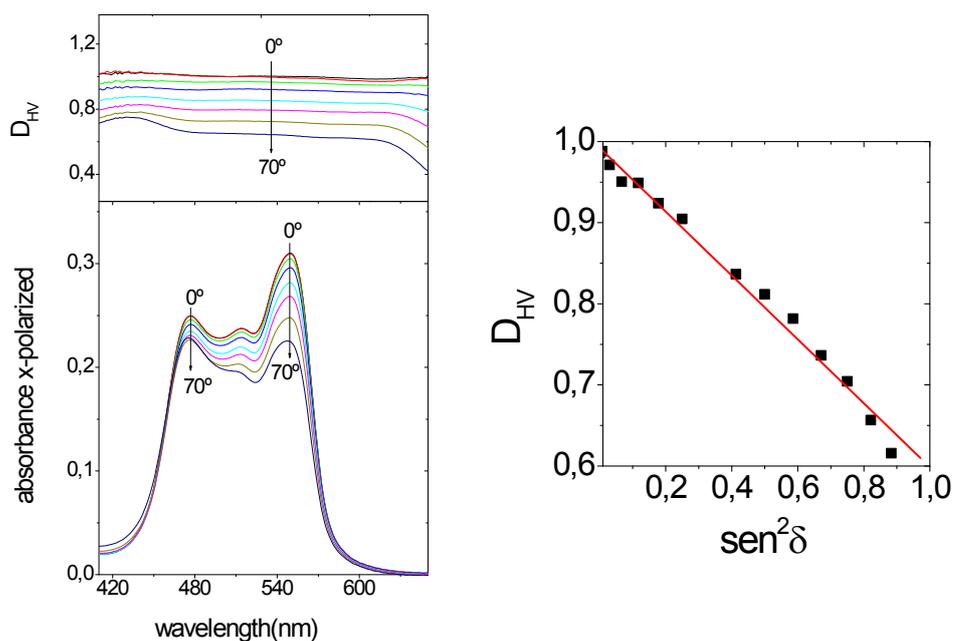
**Figure S5.** (Left) Evolution of the dichroic ratio of a 3.8% CEC PY/Lap thin film for different orientations of the sample with respect to the incident beam and X-polarized absorption spectra recorded from 0° to 60° every 10°. (Right) The linear relationship between the dichroic ratio with the twisted  $\delta$  angle at the absorption maximum.



**Figure S6.** (Left) Evolution of the dichroic ratio of a 3.7% CEC PY/Sap thin film for different orientations of the sample with respect to the incident beam and X-polarized absorption spectra recorded from  $0^\circ$  to  $50^\circ$  every  $10^\circ$ . (Right) The linear relationship between the dichroic ratio with the twisted  $\delta$  angle at the absorption maximum.



**Figure S7.** (Left) Evolution of the dichroic ratio of a 2.4% CEC of PY and 2% CEC of surfactant of Lap thin film for different orientations of the sample with respect to the incident beam and X-polarized absorption spectra recorded from  $0^\circ$  to  $70^\circ$  every  $10^\circ$ . (Right) The linear relationship between the dichroic ratio with the twisted  $\delta$  angle at the absorption maximum.

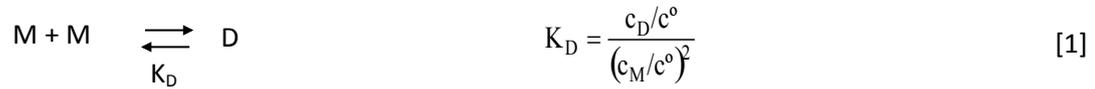


**Figure S8.** (Left) Evolution of the dichroic ratio of a 9.3% CEC of PY and 2% CEC of surfactant of Lap thin film for different orientations of the sample with respect to the incident beam and X-polarized absorption spectra recorded from  $0^\circ$  to  $70^\circ$  every  $10^\circ$ . (Right) The linear relationship between the dichroic ratio with the twisted  $\delta$  angle at the absorption maximum.

**Procedure to calculate the  $K_D$  and the spectrum of the dimer:**

The quantitative procedure to evaluate the aggregation constant of PY dye into Lap and films is described as follows:

The formation of a dimer is firstly considered in moderate dye loadings ( $\leq 10.2\%$  CEC for PY/Lap and  $\leq 20\%$  CEC for PY/Sap films). Defining the dimerization constant ( $K_D$ ) as:



where  $c_M$  and  $c_D$  are the monomer (M) and dimer (D) concentrations in equilibrium, respectively, and  $c^0$  is the standard concentration. If  $x$  is the molar fraction of the free monomer, then the equilibrium concentrations can be rewritten to the analytical concentration  $c$  by  $c_M = c x$  and  $c_D = c (1-x)/2$ . The analytical concentration of the sample is referred to the most diluted dye sample by the normalization factor ( $c = \sigma c_0$ ).

The concentration-normalized  $\sigma$  factor is recounted for each sample by  $\sigma = \text{Area}/\text{Area}_0$  (area method) where the subindex “ $0$ ” refers to the corresponding parameter of the reference sample. Once the  $\sigma$  factor is known, the dye concentration ( $c$ ) for each sample is referred to that of the reference sample ( $c_0$ ) by  $c = \sigma c_0$ . The reference sample is considered that obtained by immersing the Lap or Sap film during 5 min and 15 min into a  $10^{-5}$  M solution of PY with a relative concentration of 0.5 % and 0.9 CEC% , respectively.

Therefore the dimerization constant can be expressed by

$$K_D = \frac{1-x}{2(c_0/c^0) \sigma x^2} \quad [2]$$

If the most diluted dye/clay film is considered as the standard ( $c_0 \equiv c^0$ , for a real use of the  $\sigma$  factor, *i.e.*  $\sigma = 1$  in the most diluted films), the dimerization constant will be finally given by:

$$K_D = \frac{1-x}{2 \sigma x^2} \quad [3]$$

So,  $K_D$  can be determined from the monomer molar fraction and the concentration factor ( $\sigma$ ) for moderate dye loading samples. On the other hand, the  $x$  value can be evaluated from the normalized absorbance at any wavelength by applying the Beer-Lambert law:

$$\frac{A(\lambda)}{\sigma} = \varepsilon_M(\lambda)c_0 x l + \varepsilon_D(\lambda)c_0 (1-x)l = A_M(\lambda)x + A_D(\lambda) (1-x) \quad [4]$$

where  $\varepsilon_M(\lambda)$  and  $\varepsilon_D(\lambda)$  represent the molar absorption of the monomer and of the monomer units in the dimer at the wavelength  $\lambda$ , respectively, and  $l$  the thickness of the films. The  $A_M(\lambda) = \varepsilon_M(\lambda)c_0 l$  and  $A_D(\lambda) = \varepsilon_D(\lambda) c_0 l$  terms represent the absorbance of the monomer and of the monomer units in the dimer, respectively, referred to the reference concentration  $c_0$  and the films thickness  $l$ .

Then to evaluate dimerization constant,  $K_D$ , and the dimer absorption spectrum,  $\varepsilon_D(\lambda)$ , is based on a non-linear least square method in which the best  $K_D$  and  $\varepsilon_D(\lambda)$  values are proposed to explain the evolution of the absorption spectra with the dye concentration. Taking the  $x$  value from the eq.(3) and inserting it in eq.(4), the following expression can be drawn out:

$$\frac{A(\lambda)}{\sigma} = [\varepsilon_M(\lambda) - \varepsilon_D(\lambda)]c_0 l \frac{\sqrt{1+8K_D\sigma} - 1}{4K_D\sigma} + \varepsilon_D(\lambda)c_0 l \quad [5]$$

Hence, the evolution of the normalized absorbance ( $A(\lambda)/\sigma$ ) versus the concentration factor ( $\sigma$ ) would give us the dimerization constant ( $K_D$ ) and the absorption spectrum of the dimer ( $\varepsilon_D(\lambda)$ ).

The non-linear fit, performed by the ORIGIN 6.1 software, is based in the Levenberg-Marquardt algorithm.<sup>55</sup> The fit proposes those  $K_D$  and  $\varepsilon_D(\lambda)$  values that minimize the reduced chi-square between the experimental and the fitted data at the most representative wavelengths: the main absorption band of the monomer and around the absorption wavelength of H-band in PY/Lap or J-band in PY/Sap. The fit was realized as a global

analysis at the three wavelengths:  $\varepsilon_D(\lambda_i)$  are independent adjustable parameters whereas  $K_D$  is an adjustable parameter but kinked to be a common value to all the analysis wavelengths. Both fits supply analogous values with correlation coefficients (r) close to unity, suggesting the viability of the mathematical procedure (curve fits are shown in Figure 4).

The global analysis provides a  $K_D$  for the dimer characterized for moderate loading samples, from which and applying eq.(3) and eq.(4), an absorption spectrum for the dimer can be obtained for every sample (shown in Figure 4).