Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Luminescent 3-Hydroxyflavone nanocomposites with tuneable refractive index for photonics and UV detection by plasma assisted vacuum deposition

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S1. Geometrical Configurations used for the Deposition.

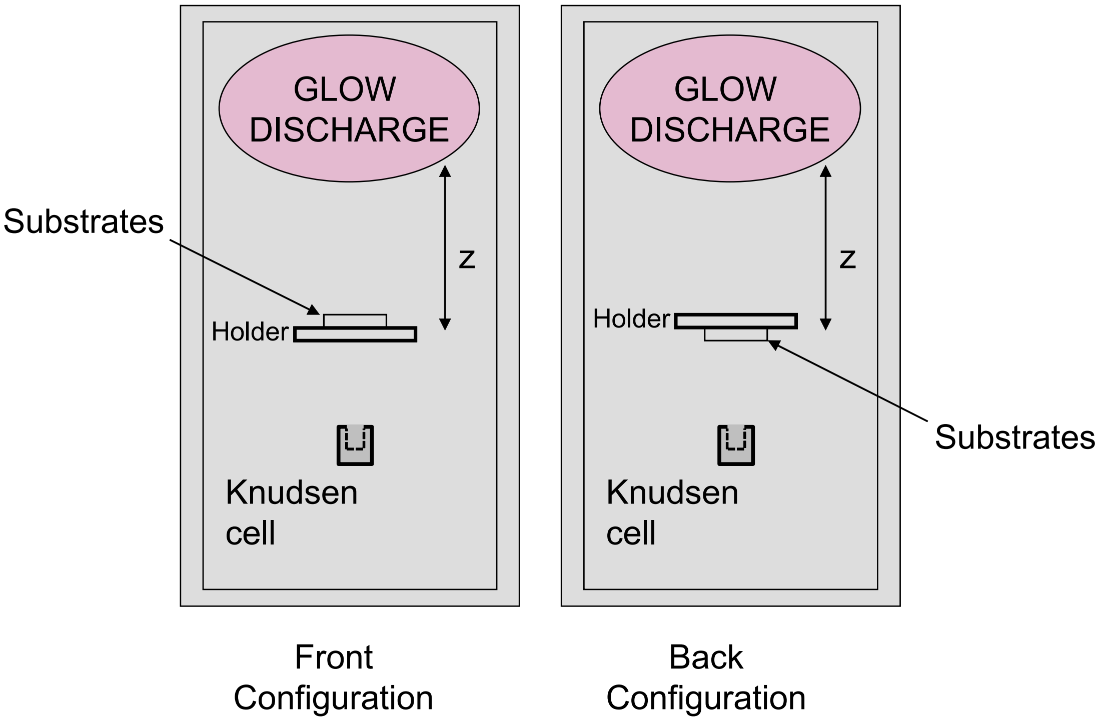

Fig. S1. Schematic representation of the front and back configurations used for the deposition of the films.

S2. Quantum yield determination.

The external quantum efficiency of the films (η) has been determined by and absolute method that makes use of a integrating sphere.[1] As indicated in Equations S1 this is calculated from the intensity absorbed by the whole system. The samples analysed in the article consist in a non-luminescent organic matrix containing luminescent dye molecules. In this system the absorption band of the dye molecules and of the plasma polymeric matrix overlap. Thus the quantum yield (Φ) of the dye molecules embedded in the films has to be calculated by applying a correction factor corresponding to the percentage of light absorbed by the active dye molecules in relation to the absorption in the whole film (Eq. S1).

$$\left.\begin{aligned} \eta = \frac{I_E}{I_{A(film)}} \Rightarrow I_E = \eta \cdot I_{A(film)} \\ \phi = \frac{I_E}{I_{A(dye)}} \end{aligned}\right\} \Rightarrow \phi = \eta \cdot \left(\frac{I_{A(film)}}{I_{A(dye)}}\right) \qquad \text{(S1)}$$

η = External radiative efficiency of the film (sphere measurement)

Φ = Dye quantum yield

I_E = Emission Intensity

$I_{A\ (film)}$ = Intensity absorbed by the whole sample

$I_{A\ (dye)}$ = Intensity absorbed by the trapped dye molecules

In order to determine the correction factor $I_{A(dye)}/I_{A(film)}$ we consider an infinitesimal layer at a depth z within the sample. Within this layer the infinitesimal intensity absorbed by the dye molecules is given by Eq. S2.

$$dI_{A(dye)} = \alpha_{dye}^{'} \cdot I(z) \cdot dz \qquad \text{(S2)}$$

Being $\alpha_{Dye}^{'}$ the attenuation or absorption coefficient associated to the dye molecules. The superscript indicates that the base *e* convection is used. I(z) is the intensity of the photon beam at a depth z within the sample. This follows the Beer–Lambert law (Eq. S3).

$$I(z) = I_0 e^{-\alpha'_{film} \cdot z}$$

(S3)

Note that α'_{film} corresponds to the absorption coefficient of the whole system (dye molecules and plasma polymeric matrix). Meanwhile I_0 is the intensity of the incident beam. By substituting (S3) in (S2) and integrating (S2) along the film thickness (t) we obtain the intensity absorbed by the dye molecules $I_{A(dye)}$.

$$I_{A(dye)} = \frac{\alpha'_{dye}}{\alpha'_{film}} \cdot I_0\left(1 - e^{-\alpha'_{film} \cdot t}\right) = \frac{\alpha'_{dye}}{\alpha'_{film}} \cdot I_{A(film)} \tag{S4}$$

Where $I_{A(film)}$ is the intensity absorbed by the film. Thus the percentage of photons absorbed by the dye molecules $I_{A(dye)}/I_{A(film)}$ is equal to the ratio between the absorption coefficients associated to the dye molecule and to whole film. This can be also expressed as the ratio between the absorbance associated to the dye molecule (A_{dye}) and the absorbance of the film (A_{film}) (Eq. S5)

$$\frac{I_{A(dye)}}{I_{A(film)}} = \frac{\alpha'_{dye}}{\alpha'_{film}} = \frac{A_{dye}}{A_{film}} \tag{S5}$$

By substituting (S5) in (S1) we obtain the expression used to determine the quantum yield of the trapped dye molecules (S6). Determination of the absorbance associated to the dye molecule (A_{dye}) is discussed in the next epigraph.

$$\phi = \eta \cdot \left(\frac{A_{film}}{A_{dye}}\right)$$

(S6)

S3. Estimation absorbance associated to the dye molecules.

As can be observed in Fig. S2 the absorption band of the dye molecule is superimposed on a continuous UV absorption that is related to the π → π* transition in the unsaturated bonds of the polymeric matrix. In order to determine the absorbance associated to the dye molecule trapped within the films, we have estimated, for each sample, a transmittance spectra corresponding to the non-luminescent polymeric matrix that contains the dye molecules. In Fig. S2 is presented, as example, the transmittance function (T_M) assumed for the polymeric matrix of sample 3HF-6. According to the formula (S7) derived from the Beer-Lambert law, the ratio between the transmittance of the sample T_{film} and the transmittance of the polymeric matrix T_M provides the absorbance $A_{3\text{-}HF}$ associated to the luminescent 3-HF molecules embedded in the film.

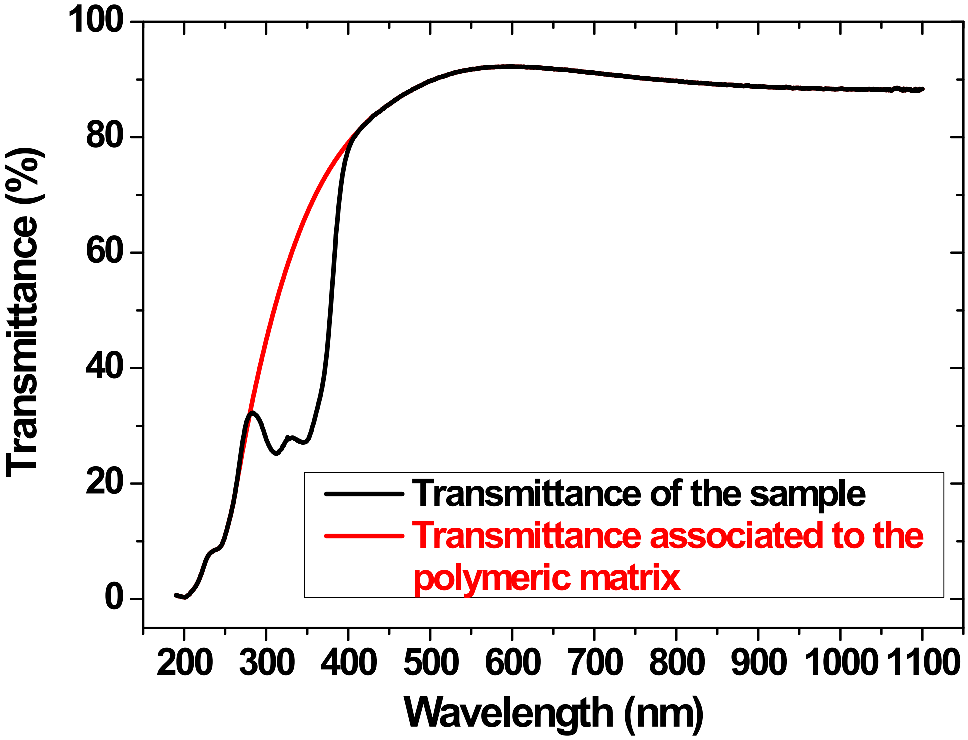

Fig. S2. Transmittance spectrum associated to the non-luminescent polymeric matrix where the 3-HF molecules are embedded.

$$A_{dye} = log_{10}\left(\frac{T_{film}}{T_M}\right) \tag{S7}$$

S4. Attribution of IR features.

Table S1. IR bands observed in the 3-HF powder spectrum.[2-7]

Position (cm^{-1})	Group	Vibration Mode
3210	–O-H C-H_x	Stretching
1609	C=O	Stretching
	C=C	Skeletal vibration in the aromatic rings
1561	C=O	Stretching
	C=C	Skeletal vibration in the aromatic rings
1481	C=C	Skeletal vibration in the aromatic rings
1463	C=C	Skeletal vibration in the aromatic rings
1418	–OH	Bending
	C-H	In plane bending
1352	–OH	In plane bending
1307	–OH	Bending
	C-H	In plane bending
1284	–OH	Bending
	C-H	In plane bending
1211	C-OH	Stretching
	C-H	In plane bending
1129	C-H	In plane bending
1077	C-H	In plane bending
1035	C-H	In plane bending
989	C-C	Deformation
896	-OH	Bending
	C-C	Deformation
780	C-H	Out of plane bending of 4 adjacent H

760	C-H	Out of plane bending of 4 adjacent H
706	C-O-C	Stretching
	C-C	Deformation
688	C-O-C	Stretching
	C-C	Deformation

Table S2. Additional bands in the IR spectra of the PAVD films.[6,8,9]

Position (cm^{-1})	Group	Vibration Mode
3350	–OH	
3065	C-H	Stretching in aromatic rings
3035	C-H	Stretching in unsaturated aliphatic groups
2960	$C-H_3$	Stretching
2935	$C-H_2$	Stretching in saturated aliphatic groups
2875	$C-H_3$	Stretching
1750	C=O	Stretching in saturated aliphatic esters
1720	C=O	Stretching in saturated aliphatic ketones and aldehydes and unsaturated esters
1700	C=O	Stretching in unsaturated groups (ketones aldehydes and carboxyls)
1650	C=O C=C	Stretching in aryl ketones Stretching in conjugated systems

S5. Excitation spectra of 3-HF containing PAVD films.

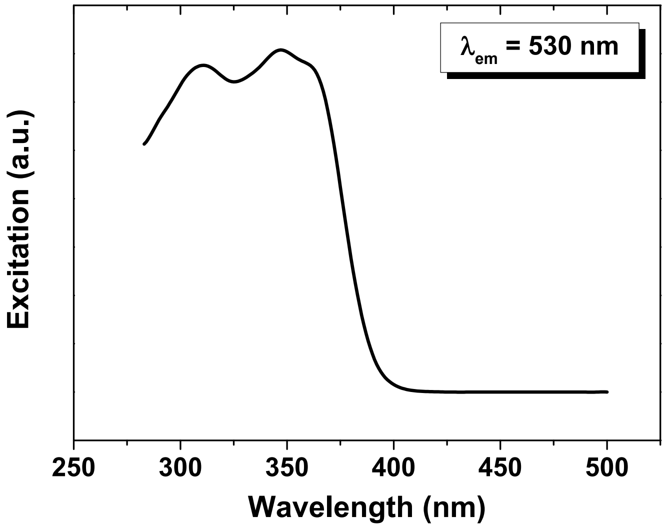

Fig. S3. Normalized excitation spectrum (λ_{ex} = 530 nm) of a 3HF-6 PAVD films.

S6. Transmission spectra of 3-HF films as a function of the thickness.

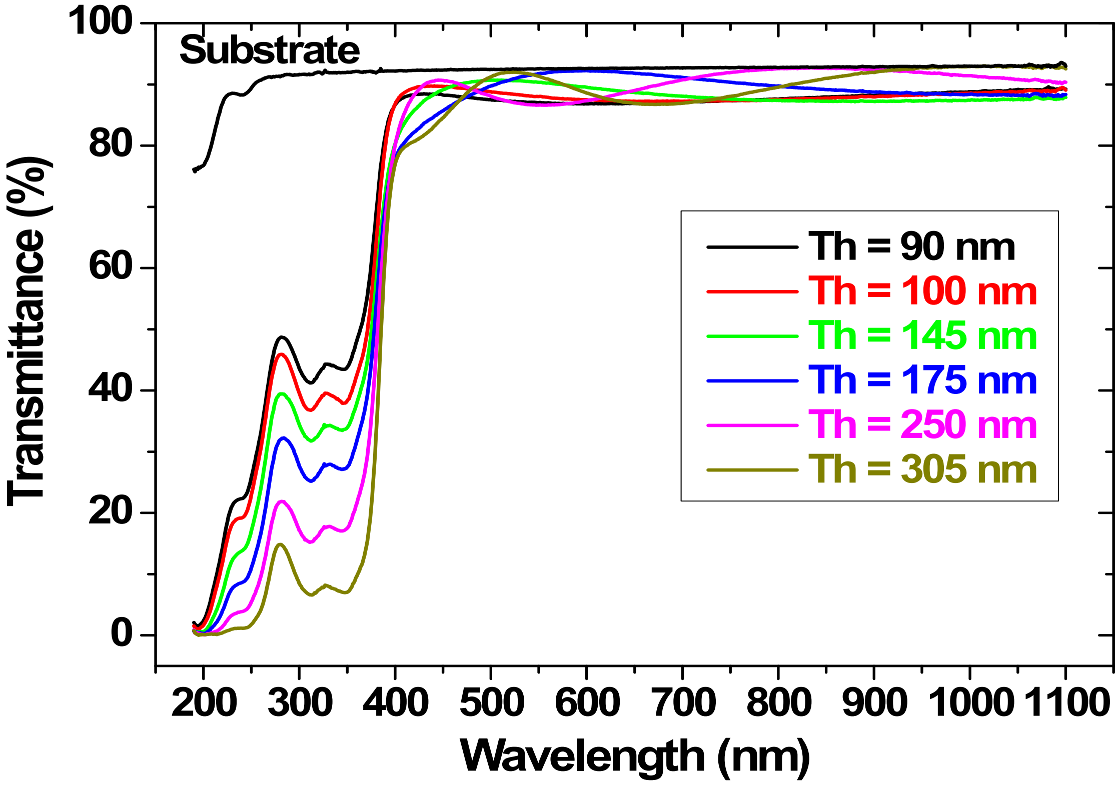

Fig. S4. UV-vis spectra of a set of 3HF-6 films (cf. Table 1 in the text) as a function of thickness. Transmittance spectrum of a fused silica substrate is also included.

S7. Relevant factors driving the quantum yield of the green emission of 3-Hydroxyflavone.

Fig. S5 shows a schematic diagram of the relevant energy levels and processes involved in the fluorescence emission of the T species of the 3-hydroxyflavone. According to it, when the molecule absorbs a UV photon it becomes promoted to the N* and from there to the T* excited state, through an ESIPT process. Once in the T* excited state, the molecule may decay to the T ground state by both radiative and non radiative process. Assuming this diagram the quantum yield of the green emission would be proportional to the efficiency of both the ESIPT and the radiative deactivation process from the T* state. Formally, we can write the following expression (S8) accounting for the two contributions:

$$\Phi \propto \Gamma_{ESIPT} \cdot \left(\frac{k_R}{k_R + k_{NR}}\right) = \Gamma_{ESIPT} \cdot \left(k_R \cdot \tau\right) \tag{S8}$$

where Γ_{ESIPT} is the efficiency of the ESIPT process, k_R and k_{NR} are the rate constants of the radiative and non-radiative decays of the T* emitting state and τ is the life time of the T emission. Note that in this expression ($k_R \cdot \tau$) provides the efficiency of the radiative decay process from the T* state.

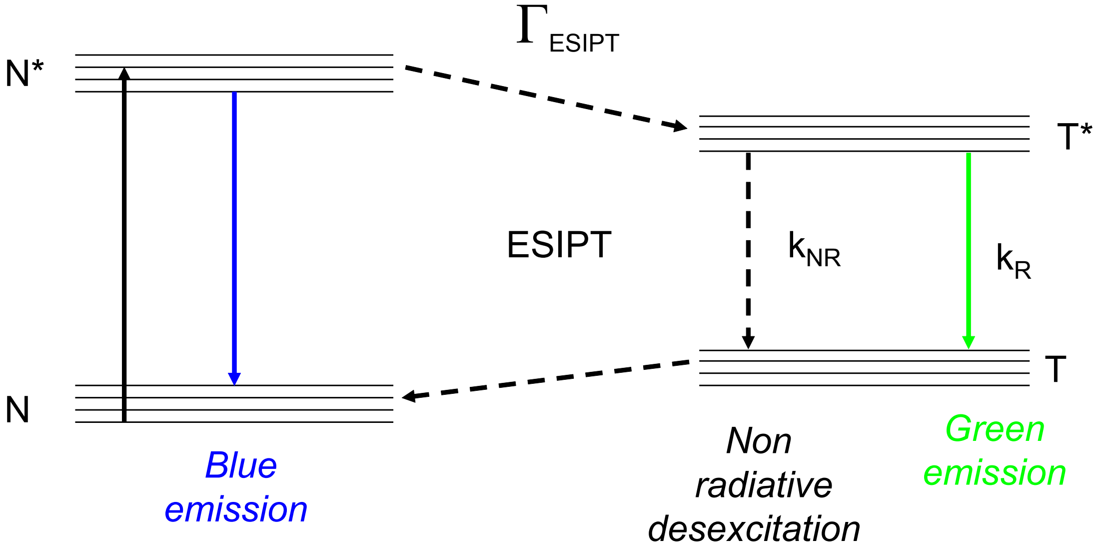

Fig. S5. Relevant energy levels and process involved in the fluorescence emission of the T specie of the 3-hydroxyflavone.

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