Electronic Supplementary Information (ESI†)

Excitation Transfer Mechanism Along the Visible to the Near-IR in Rhodamine J-Heteroaggregates

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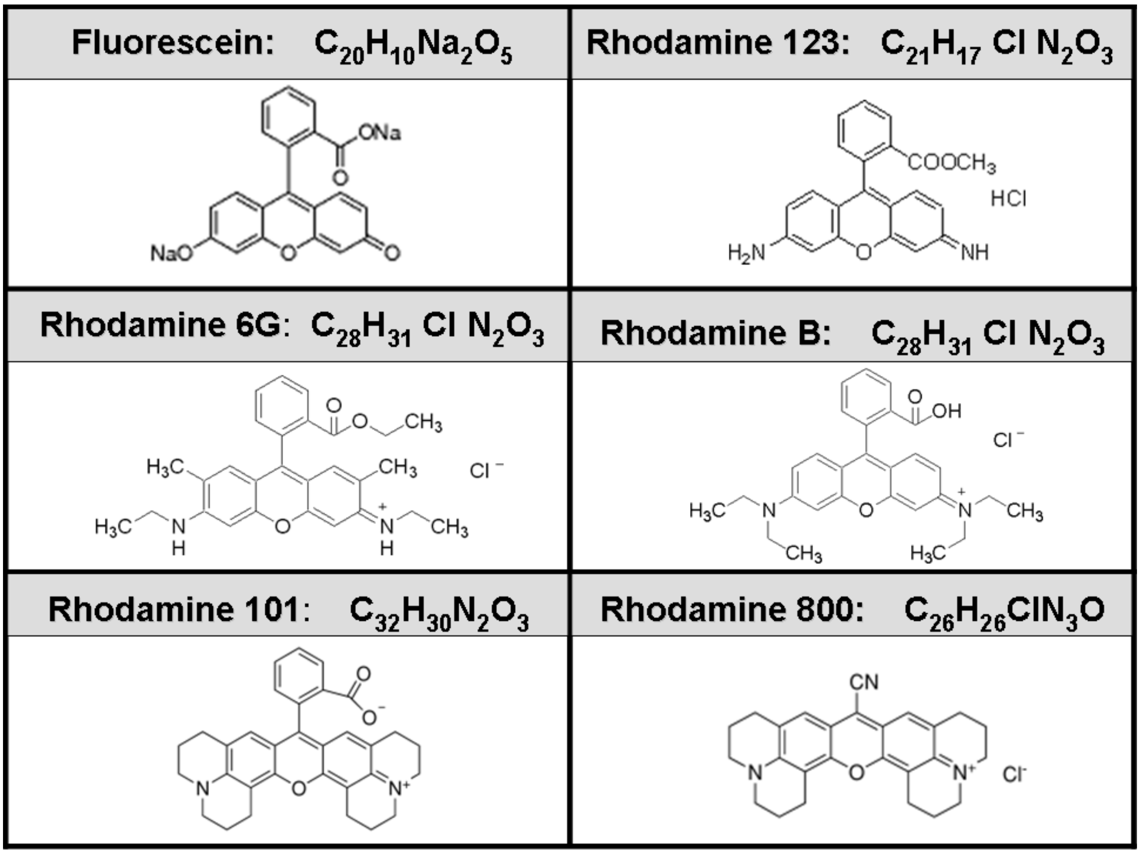

Figure S1. List and formulae of studied xanthene laser dyes (RhX).

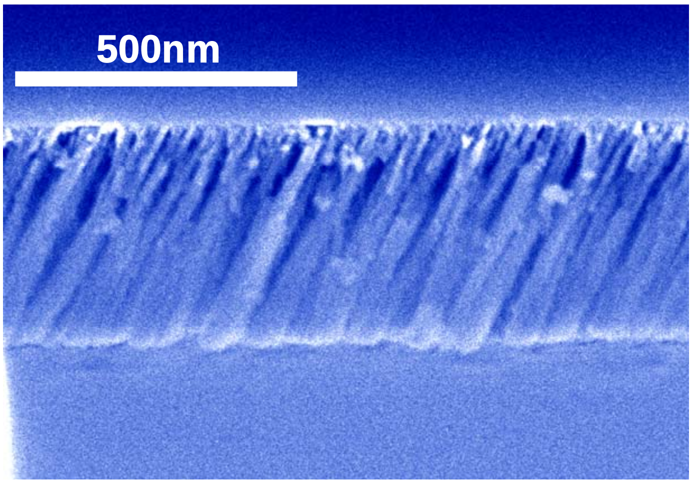

Figure S2. Cross section SEM micrograph of a SiO_2 thin film prepared by GAPVD used for the fabrication of the RhX-Rh800/SiO_2 composites.

Table S1. Calculated R_0 values for a possible RET process between the indicated dye (donor) and the Rh800 (acceptor). The emission spectra of the donor (RhX) and the absorbance spectra of the acceptor (Rh800) have been taken from diluted aqueous solutions (10^{-6} M) of each dye. The calculation has been made using the formula: $R_0^6 = \frac{9000\ (\ln 10)\ \kappa^2 Q_D}{128\ \pi^5 N\ n^4} J$ where Q_D is the quantum yield of the donor, J is the spectral overlap between the donor emission and the acceptor absorption, n is the refractive index of the media (in our case is water with n=1.33) and κ^2 is the orientation factor, that for random orientation is usually assumed $\kappa^2=2/3$.

RhX	**Q_D**	**J (10^{-13} cm^3 M^{-1})**	**R_0 (Å)**
Fluorescein	**0.92** [1]	**0.31**	**41.8**
Rhodamine 123	**0.90** [2]	**0.30**	**41.4**
Rhodamine 6G	**0.90** [1]	**0.61**	**46.5**
Rhodamine B	**0.24** [2]	**1.14**	**41.4**
Rhodamine 101	**0.93** [2]	**2.13**	**57.7**

(1) D. Magde, R. Wong, P. G. Seybold, Photochemistry and Photobiology, 75 (2002), 327.
(2) D. Magde, G.E. Rojas, P.G. Seybold, Photochemistry and Photobiology, 70 (1999) 737.

Table S2. Concentrations of Rh6G and Rh800 in the Rh6G-Rh800/SiO$_2$ composite thin films prepared by infiltrating the Rh6G at the indicated pHs. The quantitative evaluation of the amount of dye molecules incorporated within the films has been carried out by extracting the molecules with ethanol and comparing the intensity of the absorption bands of the corresponding solutions with those of standard calibrating ethanol solutions. The values obtained correspond to films of 400 nm thickness. Additional details can be founded in Reference 6 of the MS.

Sample (pH)	Rh6G concentration (10^{-12} mol cm^{-2} nm^{-1} = 10^{-2} M)	Rh800 concentration (10^{-12} mol cm^{-2} nm^{-1} = 10^{-2} M)
3	2.55	0.77
4	4.19	0.96
5.5	6.90	1.44
7	7.74	1.53
8.5	10.70	1.17
10	19.16	1.22

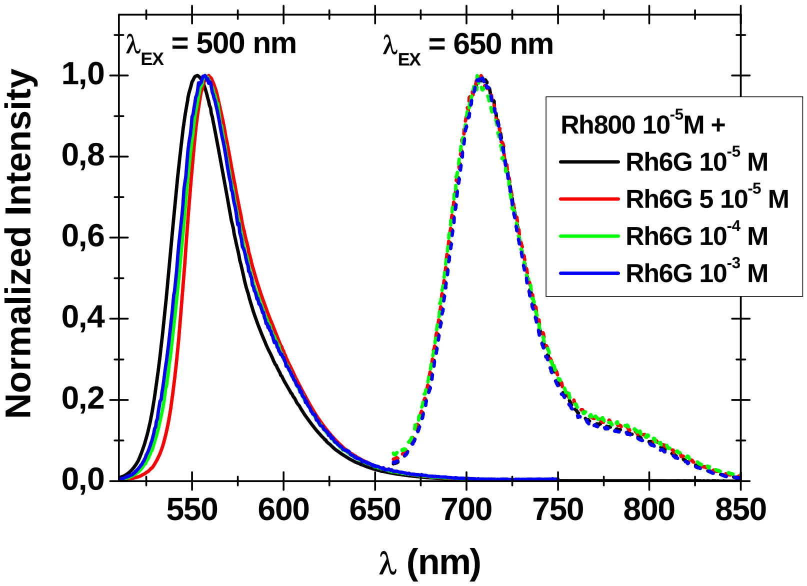

Figure S3. Fluorescence spectra of aqueous mixed solutions containing a concentration of 10^{-5} M of Rh800 and the indicated concentrations for the Rh6G. The spectra have been excited at λ_{EX}=500 (solid line) and λ_{EX}=650 nm (dashed line). It can be noted the absence of fluorescence band in the NIR when using λ_{EX}=500 nm.

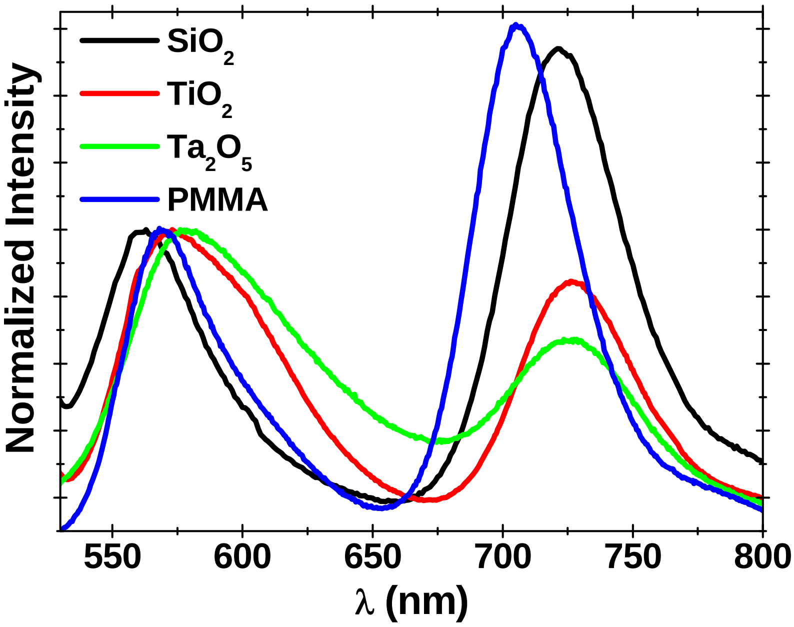

Figure S4. Normalized fluorescence spectra of Rh6G-Rh800 dye molecules incorporated in SiO_2 (black), TiO_2 (red) and Ta_2O_5 (green) GAPVD thin films and PMMA (blue) thin film deposited by spin coating. In all the matrices can be seen the Rh800 fluorescence emission band using an excitation wavelength of λ_{EX}=520 nm.

Experimental Section

Composite RhX-Rh800/SiO_2 thin films were prepared by using porous SiO_2 thin films as host materials. For this purpose, transparent and amorphous films of this material were prepared by GAPVD at room temperature on quartz and silicon substrates. Evaporation was carried out in an electron bombardment evaporator by using SiO_2 pellets as a target. Stoichiometric and columnar thin films of SiO_2 were obtained by performing the evaporation in 10^{-4} torrs of O_2 by placing the substrates at a glancing angle of 70º with respect to the evaporator source. This geometry produces films with a tilted columnar microstructure. Films with a thickness ~400 nm were prepared by this method. A characteristic of these films is that they are very porous and, therefore, are characterized by low refractive index values (n smaller than that of the substrate). Additional details can be founded in Reference 6 of the MS.

The RhX-Rh800/SiO_2 composite thin films were prepared in a two step process, incorporating first the Rh800 and then the RhX. Infiltration of Rh800 was carried out by immersion of the SiO_2 films in a water solution at acid pH (pH=2.5) and a dye concentration of 10^{-4} M. RhX was incorporated in a second stage by immersion in a 10^{-4} M aqueous solution of this dye. For the Rh6G, we have modified the pH of the solutions from 3 to 10, adding defined amounts of HCl and NaOH, respectively. According to previous works (Ref. 6 in the MS), the amount of incorporated Rh6G and Rh800 molecules into GAPVD oxide thin films depend on pH, although their chemical structure and properties are not affected by this parameter. For the series of RhX, we haven't changed systematically this parameter for these other solutions but used them at the natural pH obtained when dissolving the dyes to proceed to the infiltration.

To calculate the concentration of dye molecules incorporated into the films at each pH, the composite films were immersed in a given amount of ethanol where they were kept for 20 minutes. After this time, it was observed that the films became fully transparent while the solutions presented the pink-blue color characteristic of the solutions of Rh6G and Rh800. By comparison of the absorption intensity of the solutions with that of a series of reference solutions defining a calibration line, we have been able to quantitatively assess the amount of dye molecules incorporated into the films at each pH. To make sure that the extraction was complete and that no fragments of dye molecules remained in the films, their UV-vis spectra were measured after the leaching protocol proving the absence of any absorption bands that might account for a decomposition product.

The microstructure of the SiO_2 thin films deposited on a silicon wafer was examined by Field Emission Scanning Electron Microscopy (FESEM) in a Hitachi S5200 microscope. Cross sectional views were obtained by cleaving the silicon substrates.

UV-visible absorption spectra in transmission mode were recorded with a Varian Cary 100Conc spectrometer for the thin films deposited on quartz plates. Although the absorbance is the typical magnitude used for presenting UV-vis absorption spectra of dyes in liquid solutions, we present here some spectra as the percentage of transmitted light. We have made this choice because this is the usual way of presenting these data when using optical thin films.

Fluorescence spectra were recorded in a Jobin-Yvon Fluorolog3 spectrofluorometer using grids of 2 nm for the excitation and emission and working in the front-face configuration (solid samples) or right angle (dye solutions).