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Excitation transfer mechanism along the visible to the Near-IR in rhodamine J-heteroaggregates†

Juan R. Sánchez-Valencia, Johann Toudert, Lola González-García, Agustín R. González-Elipe and Angel Barranco*

An enhanced fluorescent emission of the dye Rhodamine 800 in the Near-IR is observed in the presence of other xanthene dye molecules (RhX) when they are hosted in different matrices due to the formation of a new type of fluorescent J-heteroaggregates. This enhanced emission of the acceptor occurs despite the low spectral overlapping and the low quantum yield of Rh800.

Dilute alcoholic Rhodamine (Rh) solutions are used as a gain media in commercially available tunable dye lasers.[1] In recent years, for applications such as solid-state lasing, opto-electronics, solar cells or sensors, numerous works have intended the incorporation of Rh molecules into inorganic and organic matrices.[2] The luminescent behaviour and quantum efficiency of Rhs in solution or in solid matrices are very dependent on the agglomeration state of the molecules. Usually, depending on the hosting medium and other factors like concentration or pH, the Rh dyes can exist as fluorescent monomers or can aggregate in the form of non-fluorescent or fluorescent aggregates, called H and J-type, respectively.[3]

Excitation transfer mechanisms between different molecules are of great importance in several fields.[4] For example, in biology this type of processes are used to measure distances between two sites on a macromolecule where a donor (D) and an acceptor (A) molecule have been fixed. Most of these works are based on the long-range dipoles coupling theory developed by Förster where the efficiency of the transfer process is directly related with the spectral overlap between D emission and A absorption.

For shorter distances (below 15 Å) the Förster theory can no longer be applied because the strong dipole–dipole interaction between molecules leads to strong changes in the absorbance and fluorescence bands of D and A.[5] Under these conditions, the spectral changes can be analyzed within the frame of the exciton theory implying the formation of a ground state heterodimer.[3g] This excitonic interaction has been recently developed for the study of the so called molecular beacons used as fluorescent DNA probes.[5] The efficiency of the transfer process for heterodimers is independent of the spectral overlap,[5] and the optical behaviour of the system can not any longer be linked to the individual molecules but associated to a new entity formed by the two type of dyes.[5d]

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† Electronic supplementary information (ESI) available: Additional optical and luminescence characterizations and calculations (Figs. S1–S4, Tables 1–2) and experimental section. See DOI: 10.1039/c0cc00087f

In this communication we report a new type of enhanced fluorescent emission process occurring when mixtures of Rh800, a dye emitting in the near infrared region (NIR), and one of the following Rh molecules (RhX): Rh6G, Rh123, RhB, Rh101 and fluorescein (ESI†, Fig. S1) are hosted in a transparent and porous SiO_2 thin film (ESI†, Fig. S2) and, preliminary evaluated, in other matrices such as TiO_2, Ta_2O_5 and PMMA. The most remarkable observation for each RhX–Rh800/SiO_2 composite is that, despite the low spectral overlap between the RhX (D) emission and Rh800 (A) absorption (ESI†, Table S1) and the low quantum yield of the Rh800 (lower than 10%),[1c,d] the Rh800 emission becomes enhanced when excited through the RhX absorption.

For the preparation of RhX–Rh800/SiO_2 composites we have used as a host porous SiO_2 thin films (~ 400 nm thickness) prepared by glancing angle physical vapour deposition (GAPVD).[6] These films, deposited on a glass substrate, consist of tilted columns separated by large mesopores extending from the surface up to its interface with the substrate (*cf.* ESI†, Fig. S2). A total porosity, consisting of meso- and micropores, of approximately 35% of the total volume has been estimated for them.[6c]

To fully understand the coupling mechanism of light between Rh molecules, we first describe in detail the optical behaviour of Rh6G–Rh800 and then we generalize the observations to the other dyes. Rh6G and Rh800 present a very low spectral overlapping of 6.1×10^{-14} cm^6 mol^{-1} and a Förster distance of 46.5 Å, calculated from diluted aqueous solutions by assuming a quantum yield of 0.90 for Rh6G and an orientation factor of 2/3 (ESI†, Table S1).[4]

The Rh6G–Rh800/SiO_2 composite thin films were prepared in a two step process, incorporating first the Rh800 and then the Rh6G. Infiltration of Rh800 was carried out by immersion of the SiO_2 films in a water solution at acidic pH (pH = 2.5) and a dye concentration of 10^{-4} M. Rh6G was incorporated in a second stage by immersion in a 10^{-4} M aqueous solution of this dye at different pHs between 3 and 10 (more details can be found in the experimental section in ESI†). According to previous works[6] the amount of incorporated Rh6G and Rh800 molecules into GAPVD oxide thin films depends on the pH, although their chemical structure and properties are not affected by this parameter.

Fig. 1a shows the UV-vis transmission spectra of the different Rh6G–Rh800/SiO_2 composite thin films. Increasing the pH leads to an increase in the amount of Rh6G molecules incorporated into the films[6] (ESI†, Table S2 shows the concentration of the dyes obtained by extracting the molecules with ethanol). In addition, Fig. 1(b) and (c) show that the
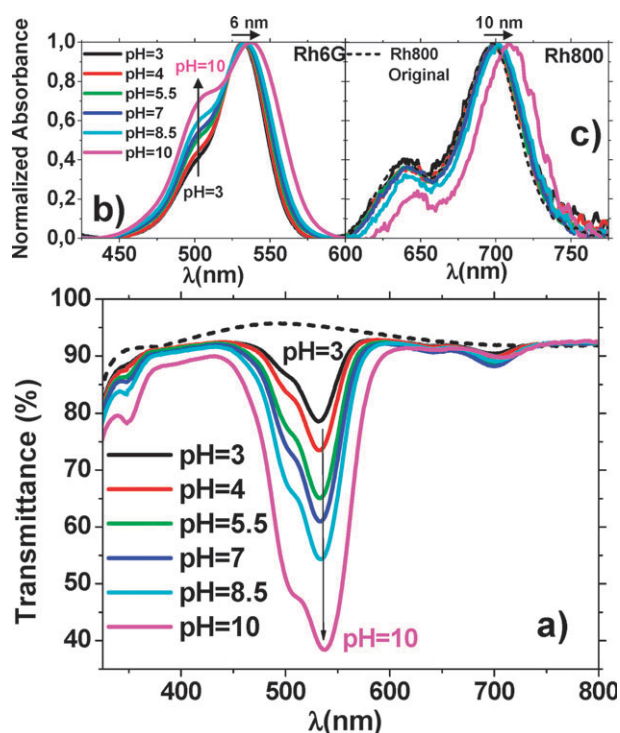
Fig. 1 (a) UV-vis transmission spectra recorded for the Rh6G–Rh800/SiO$_2$ thin films where the RhX molecule was incorporated at the indicated pHs. (b) Normalized spectra of the Rh6G and (c) Rh800 bands plotted in an absorbance scale.

shapes of the absorption spectra of Rh6G and Rh800 change with the amount of the former. For Rh6G there is a relative increase in the intensity of the shoulder at about 500 nm and a shift in the position of the maximum by about 6 nm, features usually attributed to the formation of aggregates.[3] For Rh800 the increase in the amount of adsorbed Rh6G produces a shift in the position of the maximum of about 10 nm. This change suggests that most of the Rh800 molecules are being affected by the progressive incorporation of Rh6G molecules into the film. We tentatively attribute this shift to the formation of a heteroaggregate characterized by a strong dipolar coupling between the transition moments of the two molecules that would not be compatible with a Förster mechanism.[4,5]

Fig. 2 shows the fluorescence emission spectra of the Rh6G–Rh800/SiO$_2$ composite thin films obtained by excitation at λ_{EX} = 500 (Fig. 2a) and 640 nm (Fig. 2b). The solid line plotted spectra obtained with λ_{EX}(Rh6G) = 500 nm consist of two bands at around 560 nm and 720 nm, attributed to the emission of Rh6G and Rh800 molecules, respectively. The relative intensity of the two fluorescence bands reverses with the amount of Rh6G in the film. A maximum relative intensity of the band at 720 nm is obtained for a pH = 8.5. Dashed line spectra in Fig. 2a, plotted in an enlarged scale in Fig. 2b, were recorded with an excitation wavelength λ_{EX}(Rh800) = 640 nm. In this case, the emission spectra present much lower intensities with a diminishing tendency as the Rh6G concentration in the films increases. Fig. 2(c) and (d) show the normalized fluorescence spectra obtained with λ_{EX}(Rh6G) = 500 nm. In these figures the emission spectra shift to longer wavelengths, a feature which is usually attributed to the formation of

J-aggregates.[3] In our case, a red shift of both the Rh800 absorbance and fluorescence bands is observed as the Rh6G concentration increases (cf. Fig. 1 and 2). We attribute this behaviour to the formation of Rh6G–Rh800 J-heteroaggregates in line with our previous assumption based on the absorbance spectra.[5] These heteroaggregates have a fluorescence efficiency higher than that of the adsorbed isolated Rh800 molecules (dash-doted line in Fig. 2b). In addition, the direct excitation in the Rh800 absorbance band produces a less intense fluorescence emission at ∼720 nm than by excitation through the Rh6G band. This enhancement of the emission of the Rh800 molecule can be taken as another prove of the formation of a new type of J-heteroaggregates non-reported up to date. In fact, in previously known heterodimers as those formed in molecular beacons,[5] the usual behaviour is a fluorescence quenching due to H-aggregation. To get some additional information about the characteristics of the J-heteroaggregates formed in our case, we have carried out experiments in other media with Rh6G and Rh800. Interestingly, a similar enhanced emission process was not observed in aqueous solutions containing low concentration of Rh800 and varying the Rh6G concentration (ESI†, Fig. S3). This result suggests the need of a specific and fixed geometry for the formation of the J-heteroaggregates. By contrast, results similar to those reported here were obtained by using other matrices like porous TiO$_2$ and Ta$_2$O$_5$ GAPVD thin films or PMMA coatings (ESI†, Fig. S4), thus demonstrating the need for geometrical constrains for the formation of these heteroaggregates. At this point, it is worthy of noting that the incorporation of an excess of Rh6G into the SiO$_2$ composite films, as it happens at pH = 10, produces both additional shifts in the absorption spectra (Fig. 1) and a decrease in the fluorescence intensity (Fig. 2). These features must be related with a change in the environment and a modification of the characteristics and/or number of J-heteroaggregates.

Next, we studied the series of RhX–Rh800/SiO$_2$ films whose absorption and emission spectra excited at the RhX wavelengths are shown in Fig. 3. These latter are characterized by a component at λ_{EM}(RhX) (dashed line) much smaller than that found at λ_{EM}(Rh800) (solid line). We must remind that the isolated Rh800 molecules cannot be directly excited at absorption wavelengths of RhX. Thus, the appearance of emission bands at λ_{EM}(Rh800) confirms the general character of the enhanced Rh800 fluorescence emission due to J-heteroaggregate formation.

Recently, we have studied theoretically the adsorption state of the Rh800 and Rh6G molecules on the surface of SiO$_2$ and found that while the former adsorbs with the xanthene ring parallel to the surface, the latter forms a certain angle with it due to some steric hindrance.[7] We also found that the adsorption heat of the Rh800 is higher than that of Rh6G. Taking these data into account, we tentatively propose that the xanthene ring of the Rh800 molecule placed flat on the surface of the oxide may serve as a preferential adsorption site for other Rh molecules that would tend to locate in close vicinity with the transition dipoles approximately in line. Note that this arrangement could involve more than two molecules. It is likely that the hydroxyl groups existing and/or formed on the pore surface of the host thin films during the infiltration[6]
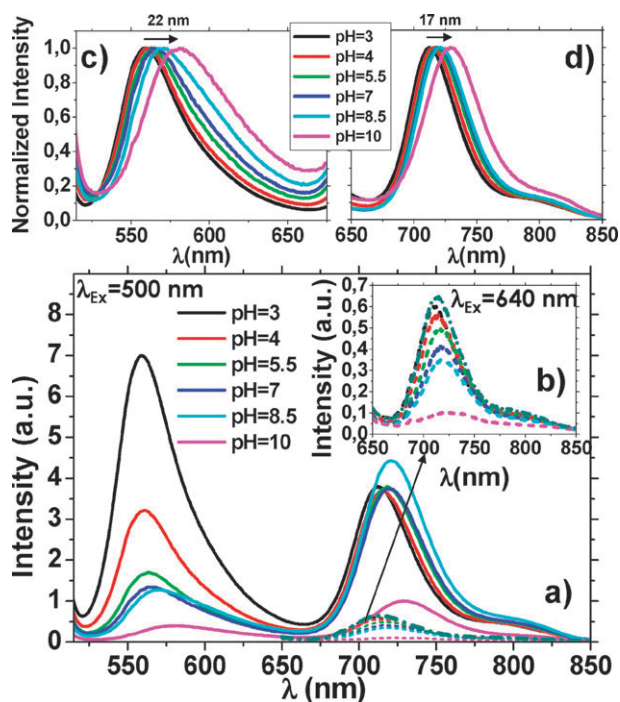
Fig. 2 Fluorescence spectra of Rh6G–Rh800/SiO2 composite thin films where the Rh6G molecule was incorporated at the indicated pHs (excitation at 500 nm (a) and 640 nm (b)). The fluorescence spectra of a Rh800/SiO2 film before the infiltration of Rh6G is also shown (dash-doted line in b)). A normalization of the fluorescence bands of Rh6G (c) and Rh800 (d) is also shown with excitation at 500 nm.
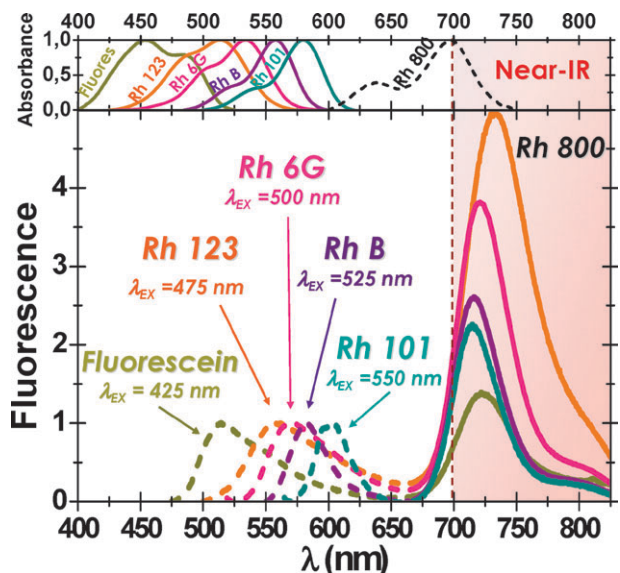

Fig. 3 Normalized absorption (top) and fluorescence (bottom) spectra, the latter referred to the intensity of Rh6G emission, recorded for the series of studied RhX–Rh800/SiO₂ thin films. Dashed and full lines correspond to bands attributed to the emission from the RhX and Rh800 molecules, respectively.

favour the formation of RhX–Rh800 J-heteroaggregates at intermolecular distances much shorter than those usually considered for a conventional Förster distance.[4] It is important to stress that the molecular nature of the interaction observed

in different matrices cannot be ascribed to a specific environment. The high air stability of our RhX–Rh800/SiO₂ composite thin films (tested for a period of up to 3 years) and their high optical quality (*i.e.*, high transmittance) make these materials suitable for integration as active optical components in robust photonic devices such as wavelength shifters, solid state lasing or other related purposes. It is important to stress that by the reported transfer process it is possible to shift the wavelength of light by a large magnitude (*e.g.* up to ∼300 nm or 1.2 eV in Fig. 3). The large and "à la carte" wavelength shifts attainable by combining Rh800 with different RhX molecules permit a tailored processing of materials for specific photonic applications. Particularly, the emission of the Rh800 at NIR wavelengths is a valuable characteristic for many practical applications based on the use of common commercial detectors and systems.

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