Fluorescence Resonance Energy Transfer between Organic Dyes in Presence and Absence of Nano Clay Laponite

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Abstract
This communication reports the phenomenon of FRET observed in between the binary solution of two dyes Acriflavine (donor) and Rhodamine B (acceptor), with and without nano-clay (laponite). It was observed that presence of clay particles increases the energy transfer efficiency. The effect of acceptor concentration on the total energy transfer efficiency has been studied to quantify the energy transfer, which may be used for photon emission and enhancement in lasing efficiency.

Keywords: Rhodamine, laponite, acriflavine, FRET

1. Introduction:
Fluorescence resonance energy transfer (FRET) is an electrodynamic phenomenon occurs through the transfer of exited state energy from donor (D) to acceptor (A) [1-3]. This nonradiative energy transfer occurs as a result of dipole-dipole coupling between the donor and the acceptor, and does not involve the emission and reabsorption of photon. The rate of energy transfer depends upon the extent of spectral overlapping area of the emission spectrum of donor with the absorption spectrum of the acceptor, the relative orientation of the donor and acceptor transition dipoles and the distance between these molecules [3]. Nonradiative energy transfer is primarily dependent on the D-A distances. Due to its sensitivity to distance, FRET has been used to investigate molecular level interaction [2-4].

FRET mechanisms are also important in other phenomenon, such as photosynthesis kinetics, chemical reactions and Brownian dynamics [1]. Fluorescence emission rate of energy transfer has wide applications in biomedical, protein folding, RNA/DNA identifications and their energy transfer process [5-6]. Another important application of FRET phenomenon is in dye lasers. If a dye laser has to be used as an ideal source, its spectral region needs to be extended. The use of such energy transfer in dye lasers is also helpful in minimizing the photo quenching effects and thereby increasing the laser efficiency [7].

Clay mineral particles play an important role in concentrating the dye molecules onto their surfaces. This may provide a platform for closer interaction between energy donor and acceptor for making energy transfer possible, in contrast to inactive systems based homogeneous solutions [3].

In our present communication, the FRET phenomenon between two dyes has been reported. Here we used two cationic dyes namely, Acriflavine and Rhodamine B as donor and acceptor respectively. We have investigated this phenomenon in water and clay dispersion solutions. These two dyes Acriflavine and Rhodamine B are in principle suitable for FRET [3]. Both the dyes are highly fluorescent. The fluorescence spectrum of acriflavine sufficiently overlaps with the absorption spectrum of Rhodamine B [see inset of fig. 1a]. The aim of this study was to investigate the FRET efficiency between these two dyes in presence and absence of nano clay laponite.

2. Experimental
Acriflavine and Rhodamine B were purchased from Sigma Chemicals Co., USA and used as received. The dyes used in our studies are positively charged and the laponite particles are negatively charged. The clay mineral used in the present
work was Laponite, obtained from Laponite Inorganic, UK and used as received. The dyes were dissolved either in water or HPLC grade methanol [Aeros Organics, USA]. The size of the clay platelet is less than 0.05 m and CEC is 0.739 meq/gm. The clay dispersion used was of 110 mg/100 ml of laponite stirred for 24 h in Milli-Q ultrapure water (electrical resistivity 18.2 Mcm-1) with a magnetic stirrer. UVvis absorption and fluorescence spectra of the solutions were recorded by a UV-Vis Spectrophotometer (Lambda-25, Perkin Elmer) and Fluorescence Spectrophotometer (LS-55, Perkin Elmer) respectively. The excitation wavelength was 420 nm.

3. Results and Discussion
In order to investigate the FRET between ACF and RhB, the fluorescence spectra of the pure and mixed dyes in solution were measured. Figure 1(a) shows the fluorescence spectra of pure ACF, pure RhB, ACF & RhB mixture. The excitation wavelength was 420 nm and was selected approximately to excite the ACF molecules directly and to avoid or minimize the direct excitation of the RhB molecules. The ACF fluorescence spectrum (curve 1) possesses a prominent band at about 500 nm. A less intense weak emission band at about 575 nm is obtained for pure RhB (curve 2). Under these circumstances we can say that prominent emission from RhB may be possible only after excitation via energy transfer from the ACF molecule.

The ACF & RhB mixture (50:50 volume ratio) fluorescence spectrum (curve 3) possesses bands at 500 nm and 575 nm which are due to the ACF & RhB monomer respectively. The ACF fluorescence band is lower and RhB fluorescence band is higher compared to their pure counterparts. A red shift of RhB fluorescence band of the order of 8 nm occurred. Such smaller shift in RhB fluorescence in montmorillonite and Hectorite were reported and attributed to monomer fluorescence of RhB adsorbed on the external clay surface or in the interlamellar regions of clay sheets [7].

The interesting thing is that here RhB emission band becomes significant due to the decreases in ACF fluorescence in favour of RhB fluorescence. In this case the emission from ACF decreases and the energy is transferred from ACF (donor) to RhB (acceptor). This transferred energy excites more electrons followed by light emission from the RhB, which is added to the original emission of RhB. As a result the intensity gets sensitized. In presence of clay (curve 4, fig. 1a) the donor fluorescence intensity decreases more in favour of acceptor fluorescence intensity resulting an increase in energy transfer efficiency.

It is interesting to mention in this context that Fluorescence resonance energy transfer (FRET) process is very sensitive to distances between the fluorophore (donor-acceptor) and occurs only when the distance is of the order of 1-10 nm [4]. In the present case clay particles play an important role in determining the concentration of the dyes on their surfaces or to make possible close interaction between energy donor and acceptor components in contrast to inactive system based on homogeneous solution.

The fluorescence spectra of ACF & RhB mixture in presence of clay for different mixing ratio are shown in fig 1b. From the figure it is observed that the RhB fluorescence increases with the increasing amount of ACF (donor) [7]. The RhB fluorescence intensity is maximum at a maximum donor amount. The energy transfer efficiencies have been calculated for various dye concentrations [3]. It was observed that FRET efficiency increases in presence of clay particles. The plot of FRET efficiency as a function of acceptor concentration in presence of clay has been shown in the inset of figure 1(b). The FRET efficiency increases with increasing acceptor concentration.
and was maximum at 99% of RhB concentration. When the RhB concentration was less than 50%, the FRET was inconsistent.

4. Conclusion
FRET between two laser dyes ACF and RhB has been demonstrated successfully in presence and absence of nano clay platelets laponite. Efficient Energy transfer does not normally takes place in dilute dye solution due to their large distance between molecules. However, energy transfer efficiency increases in presence of clay. The introduction of clay actually reduces the intermolecular separation between the donor-acceptor pair, which helps in maximum energy transfer. It has been observed that the FRET efficiency increases with increasing acceptor concentration in the mixed systems. The FRET efficiency was maximum for RhB concentration of the order of 99%.

5. References

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