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Analysis of dual peak emission from Rhodamine 6G organic dyes using photoluminescence

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Abstract. Rhodamine 6G (R6G) or Rhodamine 590 is a cationic dye with a strong absorption in the visible and a high fluorescence yield. R6G is commonly used as a tracer dye in water to determine the rate and direction of flow and transport. Some examples of Rhodamine dye applications are fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy, etc. In this work, the optical properties of R6G with various concentrations in water were observed by mean of photoluminescence (PL) measurement. The experimental results showed that the higher the concentration, the greater the intensity of the photoluminescence. It is observed that R6G dye emission spectrum had two distinctive peaks, at 550 nm and 602 nm wavelengths. R6G dye concentration affected these peaks in a very interesting manner. With the increasing R6G concentration, the emission peak shifted from 550 nm, which is dominated by monomer, to 602 nm, which is dominated by dimer emission. Our findings have given a good clue in optimizing the concentration of R6G dye in order to give the best emission for various applications.

1. Introduction
Rhodamine 6G (R6G) or Rhodamine 590 is a highly fluorescent rhodamine family dye. R6G has a chemical formulas \( C_{28}H_{31}N_2O_3Cl \). The structure of the R6G molecule is illustrated by figure 1.

![Chemical structure of Rhodamine 6G](image)

Figure 1. Chemical structure of Rhodamine 6G.

R6G is a cationic dye with a strong absorption in the visible and a high fluorescence yield. The molecule consists of two chromophores, a dibenzopyrene chromophore (xanthene) and a
carboxyphenyl group tilted by about 90° with respect to the xanthene ring (see figure 1). The π-systems of the two chromophores of R6G are therefore not conjugated. The strong absorption of R6G in aqueous solution has a maximum of around 530 nm and a vibronic shoulder of around 470 nm [1]. R6G has a molar mass of 479.02 g/mol and 1.26 g/cm³ in density. Its solubility is 20 g/l in water at 25°C and 400 g/l in methanol. R6G is commonly used as a tracer dye in water to determine the rate and direction of flow and transport. Some applications of rhodamine dye are fluorescence microscopy, flow cytometry, fluorescence correlation spectroscopy, etc. In other application, R6G is frequently used as a gain medium in dye-lasers [2]. The absorption of R6G ranges between 440 nm and 570 nm, with the peak at 530 nm [3, 4]. The resulting emission spectrum vary from about 510 nm to around 710 nm with the peak at 550 nm depending on the solvent and the dye concentration. However, the laser emission range is much narrower, from around 560 nm to 610 nm with the peak wavelength at around 575 nm [3, 5].

The color emission of R6G will change according to the levels of concentration. Molecular aggregates of R6G, in the form of dimers or higher aggregates, act to quench fluorescence and therefore degrade the lasing ability of dye–laser systems. This quenching process is largely due to the transfer of excitation energy between monomers and aggregates, which then decay non-radiatively. Dimers, in particular, are known to have a low quantum yield and so will effectively quench emission [6-8]. Dimerization comes about as the concentration of dye is increased beyond some critical value. In methanol and ethanol, R6G monomers present alone up to concentrations on the order of 0.1 mol/L, whereas in aqueous solutions, R6G begins to form dimers at concentrations as low as 1×10⁻⁵ mol/L. In aqueous solutions, the R6G dimer consists of two dye molecules bridged by a water molecule. Because of the resulting fluorescence quenching, R6G in water is not able to exhibit lasing for concentrations greater than approximately 1×10⁻⁶ mol/L [9].

The purpose of this work was to use photoluminescence (PL) to study and explain the color evolution that occurs in R6G due to changes in concentration. In this study, the excitation wavelength used was 532 nm, which was not located at the maximum absorption of R6G. This excitation wavelength was close to the 550 nm peak which was alleged as the monomer peak of R6G. Therefore, the shorter wavelength was used to facilitate analysis in determining excitation values.

2. Methodology

The experimental set-up for this work is shown in figure 2. Analysis of dual peak emission from R6G was done by focusing laser beam into a cuvette, from which then the reflected beam was collected and detected by an optical spectrometer. Observation was then made on the optical spectrum produced.

A series of aqueous R6G solutions were prepared with concentrations ranging from 10⁻⁹ to 10⁻³ g/ml. For this purpose, a concentrated solution was initially prepared and the other samples were prepared by dilution of a small volume of this stock solution in distilled water. Between 10⁻⁶ and 10⁻⁴ g/ml, more samples were prepared in smaller increments, i.e.; 2×10⁻⁶, 4×10⁻⁶, 8×10⁻⁶, 1×10⁻⁵, 2×10⁻⁵, 4×10⁻⁵ and 8×10⁻⁵ g/ml to see more detailed changes in their emissions.

For each measurement, a glass cuvette was filled with dye solution and illuminated by a picosecond laser. The laser beam was focused into the cuvette and the reflected beam from the cuvette was then collected using two collimated lenses as shown in figure 2. The emission spectrum was recorded by Ocean Optics SpectraSuite HR2000. The emission scans were performed from 400 to 700 nm.
3. Results and Discussion

Figure 3 gives an overview of the emission spectra from the aqueous dye solutions at the concentrations of $10^{-3}$ and $10^{-9}$ g/ml.

![PL spectra for R6G concentration at $10^{-3}$ and $10^{-9}$ g/ml.](image)

Based on the graph, it appears that there is a shift in the emission peak of R6G from low to high concentration. The black graph shows the spectra of R6G at a concentration of $10^{-9}$ g/ml, while the blue graph is the result of R6G spectra at a concentration of $10^{-3}$ g/ml. There were several peaks appeared in the spectra of $10^{-9}$ g/ml R6G, in contrast to one-peak-only in R6G spectra at a concentration of $10^{-3}$ g/ml. In order to prove that there was truly a shift in emission peak, this experiment was conducted on R6G samples with concentrations between $10^{-6}$ and $10^{-4}$ g/ml. For a more detailed analysis, the individual spectra for R6G with concentrations ranging from $10^{-6}$ to $10^{-4}$ g/ml are displayed in Figure 4. The high concentration solutions emitted light with peak wavelengths beyond 602 nm, while the low concentration emission was at 550 nm. A particularly interesting feature was the change in the band shape of the fluorescence emission. For intermediate concentrations, the spectral shape indicated the existence of two bands overlapping with each other [3]. The two spectral bands observed originated from R6G monomers and dimers. At a high concentration, the R6G molecules arranged themselves in so-called H-type and J-type dimers or larger...
aggregates, the first of which was energetically favored. This dimer formation influenced the electronic structure and as a consequence, the optical properties result in an emission around 600 nm. At a low dye concentration, most dye molecules were isolated from each other and fully solvated, hence the emission band was around 560 nm.

From figure 4, it appears that a greater concentration, the PL intensity will be even greater as well. It was also observed from the graph that there were changes in spectrum shapes with increasing concentrations, i.e. there were widening of spectrum and it looked like there were two peaks in the spectrum. So, based on this graph it can be assumed that there were monomer and dimer in each spectrum generated as mentioned above [3, 9].

![Figure 4](image)

Figure 4. PL spectrum of R6G at various dye concentration.

Figure 5 is a graph of changes in the peak PL intensity and wavelength against the changes in concentration. From the graph, it appears that the effect of concentration changes on the PL intensity produced was not linear. This was because self-absorption would strongly depend on the distance the fluorescence signal traveled inside the dye solution [5].

![Figure 5](image)

Figure 5. Peak intensity and peak wavelength as function of R6G concentration.

The effect of self-absorption was to rob signal from the emission line. As the number of emitting atoms increased, the likelihood of self-absorption also increased and there was no longer a linear
relationship between the number of emitting atoms and the measured intensity. The self-absorption effect occurred in the samples whose absorption and emission spectrum partially overlap, and different emission wavelengths undergo different processes of absorption when propagating in the samples.

In order to study the emission shift of R6G from 550 nm to 602 nm wavelengths, all emission spectra were analysed using photoluminescence to reveal that each spectra consisted of monomer and dimer spectrum. Figure 6 is one of the examples in the monomer-dimer analysis that was assumed in figure 4. Fitting analysis was performed at a wavelength range between 550 nm and 602 nm based on the peak wavelengths generated in figure 3. The green lines were the assumed monomer-dimer presences.

![Figure 6. Dual peak emission spectra of R6G.](image)

Figure 7 shows an evidence of monomer-dimer evolution that occurred in any concentration of R6G. From the graph, it appears that the intensity of the monomer dropped with the increase in the concentration of R6G, while the intensity of the dimer went up proportionally to the increase in concentration. The monomer-dimer percentage values should converge at a point close to the concentration of 4x10^-5 g/ml.

![Figure 7. Crossing curve of analysis dual peak monomer-dimmer.](image)
This experiment showed us that the emission of R6G may change in respond to a given concentration and therefore it may be tuned as desired by modifying the dye concentration accordingly. Appropriate concentration should be further studied for certain applications such as bio tagging etc. Regarding applications as source of laser (dye laser) etc., Further investigation on the peak stimulated emission that can be changed should also be carried out.

4. Conclusion
In this work, we studied the concentration effects in the fluorescence emission spectra of Rhodamine 6G. R6G concentrations were tested at concentrations ranging from $10^{-3}$ to $10^{-9}$ g/ml. Changing the dye concentration provided tunability between 550 nm at low concentration and 602 nm at high concentration. At a concentration approaching the value of $10^{-4}$ g/ml, the monomer and dimer curves crossed path and therefore proved the existence of monomer to dimer evolution in the R6G spectrum. However, when highly concentrated dye solutions were used in application such as dye lasers, strong absorption and self-absorption became problems. The results of this experiment is very useful to understand how the evolution monomer-dimer takes place in the concentration changes of R6G and to grasp the approximate value of emissions in accordance with the given concentration for applications such as bio-tagging, etc.

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