

Research Article

Spectral Properties for mixed Liquid of Rhodamine (6G & 3GO) Dyes dissolved in Chloroform

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Abstract

This research is focused on the spectral properties (absorption and fluorescence) for Rhodamine 3GO & 6G soluble in Chloroform, at different concentrations (1×10^{-5} , 2×10^{-5} , 5×10^{-5} , 7×10^{-5} and 1×10^{-4} mol/l) at room temperature. The intensity of absorption increased and fluorescence decreased while concentration increases which in agreement with Beer – Lambert Law. The absorption spectrum has been observed which taken a wide spectral range, so when increased the concentration each peaks shifted to a long wavelength for each solution. The fluorescence spectrum followed and entirely the same as absorption spectrum, so increase concentration shifted peaks to a long wavelength too. The quantum efficiency of the dissolved Rhodamine 3GO & 6G in chloroform has been calculated for the same above concentration were (96%, 89%, 87%, 73%, 67%) respectively. In addition to the radiative life time were (0.218, 0.496, 1.204, 1.513, 1.536 ns) and the fluorescence life time (0.207, 0.481, 1.144, 1.225, 1.044 ns) respectively.

Keywords: Xanthenes dye, Rhodamine, Rhodamine 3GO, Fluorescence, Quantum efficiency.

1. Introduction

Many experimental and theoretical works concerning the spectral properties of xanthene dyes were done because of their great promising results in solar concentration and nonlinear optics device applications. Rhodamine 3GO and 6G is a chromophore from a family of xanthene dyes that is commonly used as an active medium in tunable lasers due to its high fluorescence quantum yield (q_f) (M. Bahae Sheik *et al*, 1990 ; M.A Qusay *et al* , 2005; R. Madhanasundari *et al*, 2006). It also finds a wide range of applications in materials science, chemistry and biology as a sensitizer in solar cells, as a molecular probe, as an electrochemical luminescence sensitizer, as a water-tracing agent, as a biological stain, etc(M.A.Qusay *et al* , 2006; N.A. Dhinaa *et al* , 2007). Currently, it is widely accepted that the quenching occurs via internal conversion and intersystem crossing in the excited states of aggregates (e.g., dimers) of dyes in solution. Indeed, xanthene dyes can form aggregates in polar solution due to the strong electrostatic and dispersion interactions between the dye molecules. Because this mechanism is widely accepted, a large number of experimental works dealing with the synthesis of novel dye lasing materials attempt to avoid or decrease the possibility of dimer formation. It was assumed that

larger concentrations of dyes and reduced aggregate formation could be achieved via incorporating dyes into solid matrices or attaching them to polymer chains. However, many of these works ended up with lower quantum yields as compared to aqueous dyes. Therefore, it is desirable to investigate the fluorescence quenching mechanism and to analyze whether the intersystem crossing can be responsible for the low quantum yield in dimeric species. Direct experimental evidence of the fluorescence quenching via intersystem crossing in dimers is rather difficult to obtain.

Fluorescent collectors are generally referred to as an optical flat plate of glass or transparent plastic appropriately doped with fluorescent materials e.g. dyes or quantum dots. Such a plate has been proposed for sunlight collection in a fluorescent solar concentrator (FSC), since it can concentrate both diffuse and direct sunlight. Additionally, it can be used to modify the solar spectrum that is incident onto the solar cell; hence allows the light spectrum to be shifted into the region where the solar cell has high spectral response. These properties offer a potential to lower the cost of the electrical energy generated from the solar system.

Although the theoretical efficiency of the fluorescent collector (FC) has been proven to be about 90% (W.T. Caraway *et al* , 1972), the efficiencies of the systems in practice remain low. The performance of the FC is limited by several loss mechanisms. One of

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the major losses is re-absorption due to the overlap of the absorption and emission spectra which need to be understood before the performance of FCs can be improved.

This present study, is part of a continuous researches to study the spectral properties of liquid (Salafa I. Ibrahim,2012; Ali H. Al-Hamdani *et al* , 2014; Ali H. Al-Hamdani, *et al* ,2013); Ali H. Al-Hamdani *et al* , 2014) and hybrid (Ali H. Al-Hamdani, *et al* ,2010; Ali H Al-Hamdani *et al* , 2014) for xanthene dyes(6G, B, C and 3GO). Also the nonlinear properties of these dyes were evaluated (Ali H. Al_Hamdani 2013).

2. Experimental work

2.1 The solvent (Chloroform)



Systematic name: Trichloromethane

Other names: Formyl trichloride, Methane trichloride, Methyl trichloride, Methenyl trichloride, TCM, Freon 20, R-20, UN 1888

Properties: Molecular Formula: CHCl₃, Molecular Weight: 119.4 g/mole, Density:1.483 g/cm³, Melting point: 63.5 °C, 210 K, -82 °F, Boiling point: 61.2 °C, 334 K, 142 °F, Refractive index (n_D): 1.4459(M.P. Elking *et al* ,1968).

2.2 Instrument used in practical work

Absorption spectrum was measured by a (SP-8001.UV-visible spectrophotometer) by the processor (Metertech Inc). Fluorescence spectrum was measured by a (Spectrofluorometer SL174) by the processor (Elico).

2.3 Sample preparation

The preparation of dye solution and concentration different and that the isolation of appropriate amount of powdered dye in given volume of solvent used, according to the relationship

$$W = \frac{M_w V_c}{1000}$$

Where; W: Weight of the dissolved dye (gm), Molecular weight of the dye (gm/mol), V: The volume of the solvent (ml), C: The dye concentration (mol/l)

The prepared solutions were diluted according to the following equation

$$C_1 V_1 = C_2 V_2.$$

Where: C1: primary concentration; C2: new concentration; V1: the volume before dilution, V2: the volume after dilution

3. Calculation of optical properties

The spectrum of the molecular fluorescence $F(\nu)$ gives the relative fluorescence intensity at wave-number (ν), this is related to the quantum efficiency by the following equation (W.T. Caraway *et al* , 1972 ; M.P. Elking *et al* ,1968).

$$q_{fm} = \int_0^{\infty} F(\nu') d\nu' \quad (1)$$

In order to evaluate absolute quantum efficiency, we have to consider both the radiative and non-radiative processes taking place in the medium, therefore

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \sum K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} \quad (2)$$

Since $K_{fm} = 1/\tau_{fm}$ and $\tau_f = 1/(K_{fm} + \sum K_d)$ Therefore,

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} = \int_0^{\infty} F(\nu') d\nu' \quad (3)$$

$$q_{fm} = \frac{\text{Number of quanta emitted}}{\text{Number of quanta absorbed}}$$

Where, τ_{fm} is the radiation life time can be calculated using relation as follow,

$$\frac{1}{\tau_{fm}} = 2.88 \times 10^{-9} n^2 (\nu')^2 \int \epsilon(\nu') d\nu' \quad (4)$$

Where, n is refractive index of a medium, ν is wave number at the maximum absorption, and $\int \epsilon(\nu) d\nu$ is the area under the absorption spectrum curve as a function of the wave number.

4. Results and Discussion

The measurements of the absorption and fluorescence spectra of the samples are taken by using a spectrophotometer (Metertech, SP8001, UV/VIS Spectrophotometer), and the emission spectra taken by using (Spectrofluorometer-model SL174, Elico) respectively. Refractive index is measured by using refractometer (Bellingham and Stanley Ltd, Tunbridgewells, ABBE60, England). Different concentrations (1×10^{-5} , 2×10^{-5} , 5×10^{-5} , 7×10^{-5} and 1×10^{-4} mol/l) of 3GO dye dissolved in diachloform were prepared at the laboratory environments. The absorption and fluorescence spectra for a liquid sample of 3GO& 6G dye with the above concentrations were depicted in Figure,1. This figure illustrates the fluorescence spectra that were observed from the front surface of the samples with various concentrations (peak absorbance at 520-530 nm).

Table 1: The stock shift between the absorption and fluorescence spectra, the radiated, fluorescence lifetime and the quantum efficiency of fluorescence for R3GO&6G

Concentration mol/l	Absorption λ_{max}	Fluorescence λ_{max}	Stock Shift nm	Quantum efficiency %
1×10^{-5}	528	548	20	0.91
2×10^{-5}	530	550	20	0.97
5×10^{-5}	528	562	34	0.84
7×10^{-5}	522	565	43	0.75
1×10^{-4}	518	569	51	0.69

Table 2: Compression between the stock shift and the quantum efficiency for the solution of rhodamine 6G , 3GO and their mixture (6G , 3GO) dissolved in chloroform

Concentration mol/l	Stock Shift nm			Quantum efficiency %		
	R6G	3Go	mixture	R6G	3Go	mixture
1×10^{-5}	22	22	20	0.97	0.95	0.91
2×10^{-5}	24	29	20	0.93	0.97	0.97
5×10^{-5}	37	39	34	0.76	0.95	0.84
7×10^{-5}	50	44	43	0.74	0.81	0.75
1×10^{-4}	57	54	51	0.69	0.68	0.69

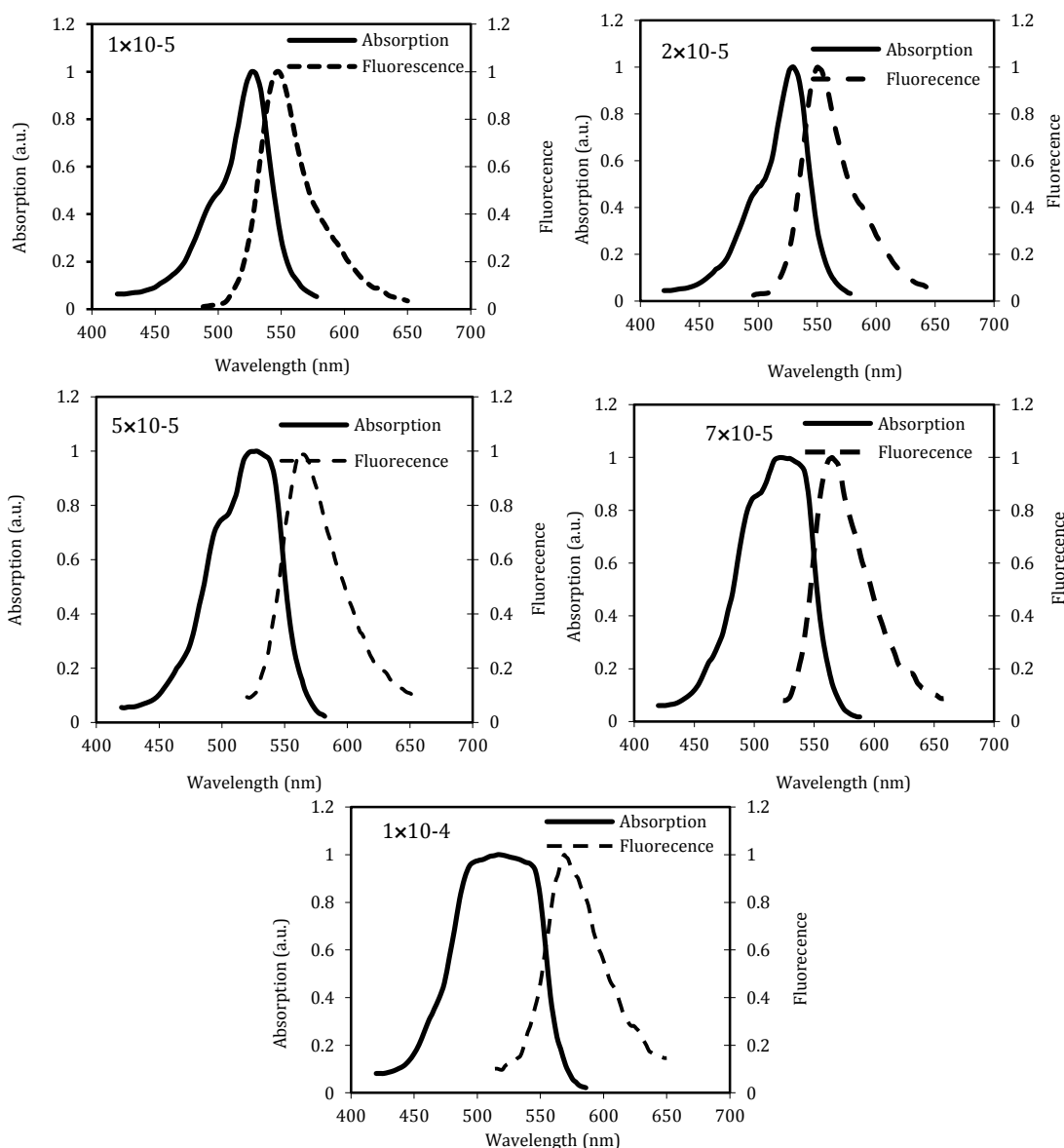


Fig.1 The fluorescence and absorption spectra for 3GO +6G dye dissolved in chloroform with different concentration(1×10^{-5} , 2×10^{-5} , 5×10^{-5} , 7×10^{-5} and 1×10^{-4} mol/l)

Although the signal tends to be red-shifted as the absorbance increases, it is crucial to point out that this shifting is no longer observed when the absorbance of the sample is less than 0.07. This key feature suggests that the spectra detected from the samples with low absorbance are not influenced by the self-absorption mechanism. These spectra, hence, are believed to be the first generation fluorescence of the material under study.

From this figure, the position of the maximum sample absorption and maximum fluorescence are indicated. The stock shift which represent the difference between the positions of the peak fluorescence and peak absorption of the dye at each concentrations are summarized in table 1.

This table indicate that as the 3Go dye concentration was increased the stock shift to the red band was increased (approximately 53%) which represent a promised results in solar cell applications (Silicon solar cell is more response to red and NIR wavelengths of the solar spectrum). Unfortunately the results include a Cruel quantum efficiencies values (approximately 28%) when the 3GO dye concentration decrease from 1×10^{-5} to 1×10^{-4} mol/l. The fluorescence life time is shown also in table 1. High fluorescence quantum yield (>0.8) is observed in solution of Rhodamine 3GO at low concentrations (10^{-4} to 10^{-5} M) whereas at higher concentrations ($>10^{-4}$ M), the quantum yield decreases rapidly to less than 0.68.

Conclusion

We have demonstrated an alternative approach to determining the collection efficiency of the typical fluorescent collectors through the determination of the fluorescence spectra observed close to the front surface. This method allows us to determine the influence of the self-absorption process at each particular wavelength by considering the fluorescent collection efficiency.

The results of this study of the Rhodamine dye solutions 3GO indicate that the best concentration was the lower one (1×10^{-5} mol/l) which quantum efficiency equal 96% for the liquid sample of 3GO dissolved in chloroform solvent. So this dye concentration can be used to improve solar cell conversion efficiency. But since the other important parameter (stock shift) was small (only 22 nm) which offer a small matching between the solar spectrum and silicon solar cell responsivity. So one conclude that there is a large leakages in the collected data about dye properties and there is a great interest must focus on this filed.

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