Optical Spectral Study of Rhodamine Dyes Mixture Solution in Chloroform

Slafa Ismael Ibrahim
Energy and Renewable Energies Technology Center, University of Technology/Baghdad
Email: chemistsulafa_59@yahoo.com
Majid Hameed Abdulmajeed
Materials Engineering Department, University of Technology/Baghdad

Received on: 21/6/2012 & Accepted on: 8/11/2012

ABSTRACT

The spectral properties (absorption and fluorescence) of laser dyes (Rhodamine6G, Rhodamine 3GO and Rhodamine B) mixture have been studied. This type of laser dye belongs to the Xanthenes family, it has dissolved in chloroform to prepare ($1*10^{-5}$ M) in different ratio such as (1R6G:1R3GO:1RB, 2R6G:1R3GO:1RB, 3R6G:1R3GO:1RB, 4R6G:1R3GO:1RB, 1R6G:2R3GO:1RB, 1R6G:3R3GO:1RB, 1R6G:4R3GO:1RB, 1R6G:1R3GO:2RB, 1R6G:1R3GO:3RB, and 1R6G:1R3GO:4RB) at room temperature.

The quantum efficiency of the dissolved Rhodamine in chloroform has been computed by using the above ratio and their results are as follows (89%,92%, 93%,95%,92%,93%,94%,84%,84%,and 84%) respectively.
The Radiative lifetime have been computed as given (0.188,0.19,0.203,0.209,0.198,0.196,0.201,0.191,0.207,and0.219ns)respectively.
Fluorescence lifetime have been also computed as given (0.167,0.174,0.189,0.198,0.182,0.183,0.189,0.160,0.174,and0.184ns) respectively.

Keywords: Xanthenes dyes, Rhodamine, Laser dye, Rhodamine 6G, Rhodamine B, Rhodamine 3GO.

دراسة الطيف البصري لمحلول مزيج صبغات الرودامين في الكلوروفورم

الخلاصة

تم دراسة الخواص الطيفية (الامتصاصية و الفلورة) لمزيج الصبغات الليزرية (رودامين 6G، رودامين 3GO، و رودامين B) . هذا النوع من الصبغات يعود إلى عائلة الزانثين ، حيث تمت إذابتها في الكلوروفورم لتحضير محاليل بتركيز($1*10^{-5}$ M) بنسب مختلفة مثل، 1R6G:1R3GO:1RB, ، 2R6G:1R3GO:1RB ، 3R6G:1R3GO:1RB، 4R6G:1R3GO:1RB ، 1R6G:2R3GO:1RB ، 1R6G:3R3GO:1RB، 1R6G:4R3GO:1RB ، 1R6G:1R3GO:2RB ، 1R6G:1R3GO:3RB وبدرجة حرارة الغرفة. الكفاءة الكمية المحسوبة للرودامين المذاب في (1R6G:1R3GO:4RB

https://doi.org/10.30684/etj.31.4B.4
2412-0758/University of Technology-Iraq, Baghdad, Iraq

الكلوروفورم باستعمال النسب أعلاه كانت كما يلي(٨٩%،٩٢%، ٩٣%،٩٥%،٩٢%،٩٣%،٩٤%،٨٤%،٨٤%و٨٤%) على التوالي.
تم حساب زمن العمر الإشعاعي وكما يلي(0.188، 0.19 ، 0.203 ،0.209 ، 0.198، 0.196، 0.201، 0.191 ، 0.207 و 0.219) نانوثانية على التوالي. كما تم حساب زمن عمر التألق وكما يلي(0.167،0.174،0.189،0.198،0.182،0.183،0.189،0.160،0.174 و0.184) نانوثانية على التوالي.

الكلمات المرشده: صبغات الزانثين، الرودامين، صبغات ليزرية، رودامين 6G ،رودامين B ، ورودامين3GO.

INTRODUCTION

The Rhodamine dyes are an art-known series of dyes, e.g., the first member of the series, rhodamine B was synthesized as early as 1887. All of the rhodamines are based structurally on xanthenes[1],which contain xanthylium as chromophore with amino or hydroxyl groups meta to the oxygen as the usual auxochromes. Rhodamines are commercially the most important amino xanthenes [2].They cover the wavelength region from 500-700nm and are generally very efficient [3].

There are large amount of data about laser dyes from many authors, Saito Y. and co-worker studies the simultaneous two- and three-band laser emissions which obtained in a process of mixing two and three kinds of dyes excited by a nitrogen laser. They were blue, green, and yellow in a coumarin 460 (C460)/disodium fluorescein (DF)/Rhodamine 610 (R61O) dye mixture, and blue, green, and red in a C460/DF/Rhodamine 640 (R640) dye mixture. Strong energy transfers from DF to R610 and to R640 were shown. R610 and R640 laser emissions on mixing with DF were obtained at very low concentrations [4]. Mekhlif H.M. study the effect of oxygen on absorption and fluorescence spectrum of two laser dyes in different solvent such as (ethanol, methanol) and found that the present of oxygen effect on fluorescence spectrum, quantum efficiency yield, and fluorescence life time[5].

Annieta P. K. and co-workers studies photosensitivity of laser dye mixtures in polymer matrix, using Polymethyl methacrylate (PMMA) films doped with Rhodamine 6G -Rhodamine B dye system [6]. Al-Khafage A.A.M. study the effect of concentration and solvent on the spectral properties of laser dye(R110), and found that there is a red-shift with increase the concentration, and blue-shift in proportion to absorption spectrum with increase the polarity of solvent[7].

Magde D. and co-workers studies the absolute fluorescence quantum yields for Rhodamine 6G cation and the fluorescein dianion dyes in nine solvents [8].

Noginov M.A. and co-workers studies the spectroscopic properties of liquid solutions of R6G mixed with a solution of aggregated silver nano particles [9].

El Mongy S.A. study the electronic and fluorescence spectra of poly styrene doped with Rhodamine 6G [10].

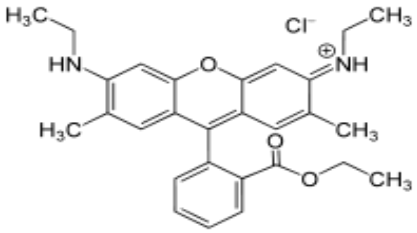
Byung J.J. and co-worker studies the efficiency improvement in a photovoltaic device by using organic buffer layer which including Rhodamine (6G, 3GO, B) and other dyes [11].

In this study we choose three kind of Rhodamine dye and study the effect of blending them in different ratio at concentration ($1*10^{-5}$M) using chloroform as a solvent on spectral properties.

EXPERIMENTAL PART

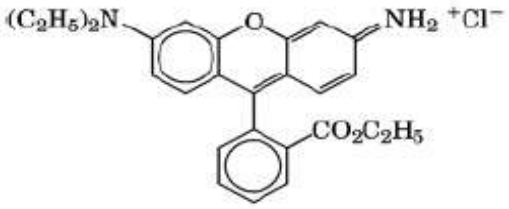
Materials and Chemicals

This work has been carried out with dyes of xanthenes derivative, Rhodamine 6G chloride which have the structure:



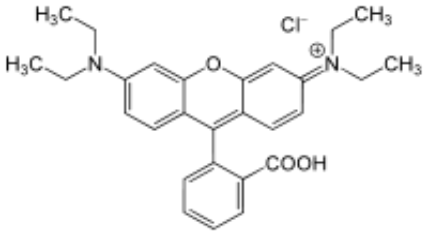
Molecular formula $C_{28}H_{31}N_2O_3Cl$, molar mass (479.02 g/mole).

Rhodamine 3GO chloride which have the structure:



Molecular formula $C_{26}H_{27}N_2O_3Cl$, molar mass (451.02 g/mole).

Rhodamine B, which have the structure:



Molecular formula $C_{28}H_{31}N_2O_3Cl$, molar mass (479.02 g/mole), HIMEDIA company, India. Chloroform was used as a solvent which purity is (99.5%), Analar company (England)**.** Electronic balance type (Denver Instrument).

Spectroscopic Measurement

The measurements of the absorption 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). Refractive index is taken by using refractometer (Bellingham and Stanley Ltd, Tunbridgewells, ABBE60, England).

Solvent (chloroform)

To study the absorption and fluorescence spectrum for the chloroform, it can be shown from Figure (1,2) that it has no absorption and overlapping at the fluorescence at the spectral range of Rhodamine dye within wavelength range (400-700nm).

Preparation of dyes:

The powder of Rhodamine dyes is accurately weighting by using analytical balances (Denver instrument, TP-214, Germany). Solutions of concentration ($1*10^{-5}$ M) of three dyes (R6G, 3GO, RB) in chloroform solvent were prepared.

Measuring of Quantum efficiency (q_{fm}):

Quantum efficiency defining as the ratio between number of quanta emitted and number of quanta absorbed:

$$q_{fm} = \frac{\text{Number of quanta emitted}}{\text{Number of quanta absorbed}} \quad \dots (1)$$

The spectrum of the molecular fluorescence F (ύ) gives the relative fluorescence intensity at wave-number (ύ); this is related to the quantum efficiency by the following equation**:**

$$q_{fm} = \int_0^{\infty} F\left(\bar{v}\right) \, d\bar{v} \qquad ...(2)$$

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

$$q_{fm} = \frac{K_{fm}}{K_{fm} + \Sigma K_d} = \frac{K_{fm}}{K_{fm} + K_{IC} + K_{ISC}} ...(3)$$

Since

$$Kfm = \frac{1}{J_{fm}} \qquad ...(4)$$

, and

$$\tau_f = \frac{1}{K_{fm} + \sum K_d} ...(5)$$

Where: K_{fm} is radiative emission probability, τ_{fm} is non-radiative life time, τ_f is fluorescence life time. Therefore:

$$q_{fm} = \frac{\tau_f}{\tau_{fm}} = \int_0^{\infty} F(\upsilon')d\upsilon' \ldots (6)$$

Radiative emission probability measurement (K_{fm})

The radiative emission probability can be determined from Bowen-wokes equation [12] by the following equation:

$$K_{fm} = \frac{1}{\tau_{fm}} = 2.88\times10^{-9}\times n^2\times(\bar{\upsilon}^2)\int \varepsilon(\bar{\upsilon})d\bar{\upsilon} \ldots (7)$$

Where:n is refractive index, ε is molar absorption coefficient, ύ is wave number.

RESULTS AND DISCUSSION

Absorption and fluorescence spectral

The absorption and fluorescence spectral for of (R6G, R3GO and RB) before mixing at concentration ($1*10^{-5}$M**)** are listed in Table (1).

The absorption and fluorescence spectral for mixtures of (R6G, R3GO and RB) at different ratio are shown in Figure (3), (4), (5), (6), (7), (8),(9), (10),(11)and(12) respectively.

From these Figures we can observed that (R 6G, R 3GO, RB mixture) solution absorption spectrum has a wide spectral range at wavelength range between (400-700nm).

For sample (1) the maximum absorption appears at wavelength (530.4nm) and red shifted by approximately (20 nm), for sample (2) the maximum absorption appears at wavelength (528 nm) and red shifted by approximately (21nm), for sample (3) the maximum absorption appears at wavelength (527.8 nm) and red shifted by approximately (20 nm), for sample (4) the maximum absorption appears at wavelength (527.8 nm) and red shifted by approximately (21 nm), for sample (5) the maximum absorption appears at wavelength(529.1 nm) and red shifted by approximately (21nm),for sample (6) the maximum absorption appears at wavelength (529.1 nm) and red shifted by approximately (20 nm),for sample (7) the maximum absorption appears at wavelength (528.5 nm) and red shifted by approximately (20nm), for sample (8) the maximum absorption appears at wavelength (542.1 nm) and red shifted by approximately (19 nm), for sample (9) the maximum absorption appears at wavelength (545.3 nm) and red shifted by approximately (19nm), for sample (10) the maximum absorption appears at wavelength (545.9nm) and red shifted by approximately (19 nm).

The absorption and fluorescence shift for samples are shown in Figure (13). The stock shift between fluorescence and absorption of samples are shown in Figure (14).

Rhodamine B dye molecules have been selected as donor. As the volume ratio of the RB is increased above that of R6G, R3GO somehow changes are introduced in the energy exchange process, the energy exchange between the three dyes is

maximum for this particular combination. This is due to the aggregation quenching in dye molecules.

The wavelength at relative maximum intensity for absorption and fluorescence of (R6G, R3GO and RB) mixtures at study stock ratio listed in Table (2).

Quantum efficiency

From the results of calculation by using computer model (Matlab 6.5), and equation (3), the result of fluorescence quantum efficiency yield is listed in Table (2), for the mixture at study stock ratio.

We can observed that the quantum efficiency yield decrease with increase the volume ratio of RB solution and increase with increase the volume ratio of (R6G,R3GO) solution, This due to the increasing in non radiative transition, which is congruous with earlier researches[13].

Radiative and fluorescence life time

From equation (9) radiative emission probability was calculated, radiative life time from equation (6) ,and fluorescence life time from equation (8),the result are listed in Table (2), for the mixture at study stock ratio. We can observed that the radiative life time and fluorescence life time increase with different volume ratio adding of Rhodamine dyes, and fluorescence life time less than radiative life time because of non radiative processes (Internal conversion ,Inter system crossing).

CONCLUSIONS

From the observations it can be concluded that:

-Increase the relative intensity with increase the volume ratio of RB, and decrease with increase the volume ratio of R6G, R3GO.

- The stock shift of mixture slightly changes with changing volume ratio.

-Increase of quantum efficiency yield with increasing the volume ratio of R6G, R3GO.

-Quantum efficiency yield of the mixture with increasing volume ratio of RB less than that of mixture with increasing volume ratio of R6G, R3GO.

-Radiative emission probability of the mixture with increasing volume ratio of (RB) is less than that of R6G, and R3GO dye.

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Table (1) the wavelength at relative maximum intensity for absorption and fluorescence for R6G, R3GO and RB.

Dye	Conc.	$ABS_{max.}$	$F_{max.}$	Stock Shift
Rhodamine 6G	$1*10^{-5}$ M	528	550	22
Rhodamine 3GO	$1*10^{-5}$ M	528	550	22
Rhodamine B	$1*10^{-5}$ M	546.6	567	20.4

Table (2) The wavelength at relative maximum intensity for absorption and fluorescence, quantum efficiency yield, radiative emission probability, radiative life time, and fluorescence life time for (R6G&R3GO&RB) mixture dyes.

Sample No.	Dye ratio	ABS max.	F.max	Stock Shift	Quantum efficiency	Kfm	τfm	τf
1	**R6G&3GO&B1:1:1**	**530.4**	**551**	**20.6**	**0.89**	**5.314**	**0.188**	**0.167**
2	**R6G&3GO&B2:1:1**	**528**	**549.5**	**21.5**	**0.92**	**5.261**	**0.19**	**0.174**
3	**R6G&3GO&B3:1:1**	**527.8**	**548**	**20.2**	**0.93**	**4.917**	**0.203**	**0.189**
4	**R6G&3GO&B4:1:1**	**527.8**	**549.5**	**21.7**	**0.95**	**4.774**	**0.209**	**0.198**
5	**R6G&3GO&B1:2:1**	**529.1**	**550**	**20.9**	**0.92**	**5.034**	**0.198**	**0.182**
6	**R6G&3GO&B1:3:1**	**529.1**	**549**	**19.9**	**0.93**	**5.076**	**0.196**	**0.183**
7	**R6G&3GO&B1:4:1**	**528.5**	**548.5**	**20**	**0.94**	**4.962**	**0.201**	**0.189**
8	**R6G&3GO&B1:1:2**	**542.1**	**561**	**18.9**	**0.84**	**5.219**	**0.191**	**0.16**
9	**R6G&3GO&B1:1:3**	**545.3**	**564**	**18.7**	**0.84**	**4.825**	**0.207**	**0.174**

10	**R6G&3GO&B1:1:4**	**545.9**	**565.5**	**19.6**	**0.84**	**4.548**	**0.219**	**0.184**

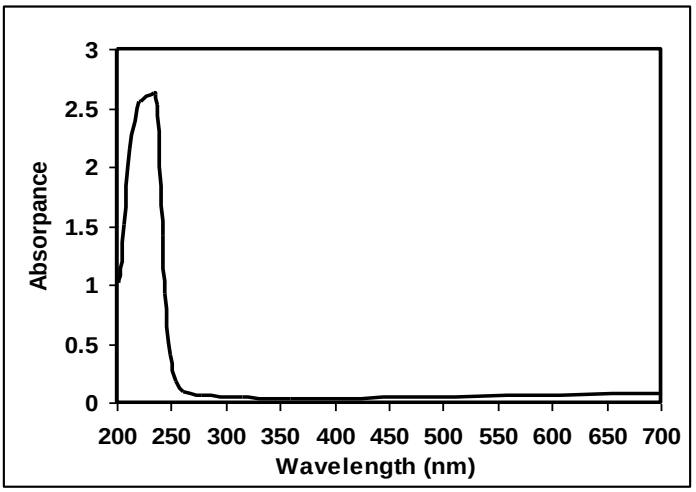

Figure (1) Absorption spectrum of chloroform.

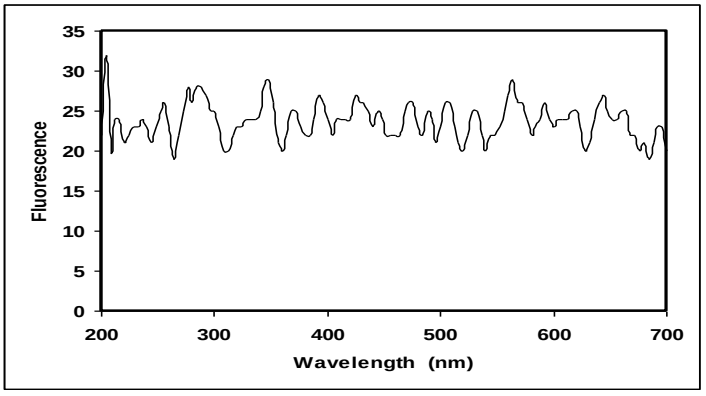

Figure (2) Fluorescence of chloroform.

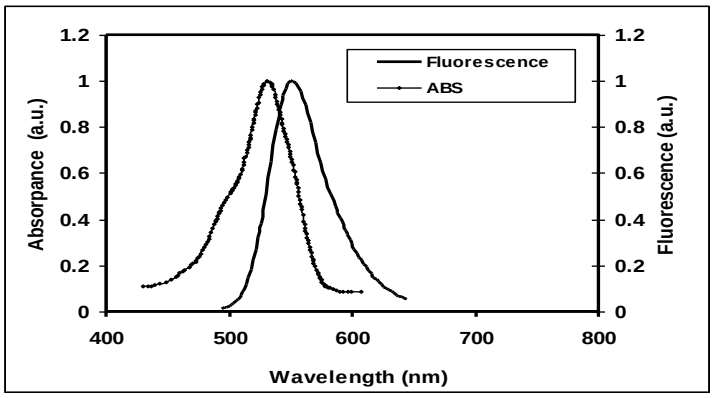

Figure (3) Absorption and Fluorescence Spectrum of R.

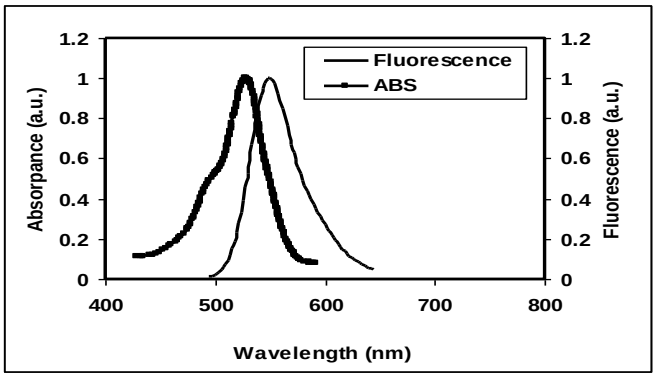

Figure (4) Absorption and fluorescence spectrum of R 6G&R3GO & RB mixture at [2:1:1] ratio.

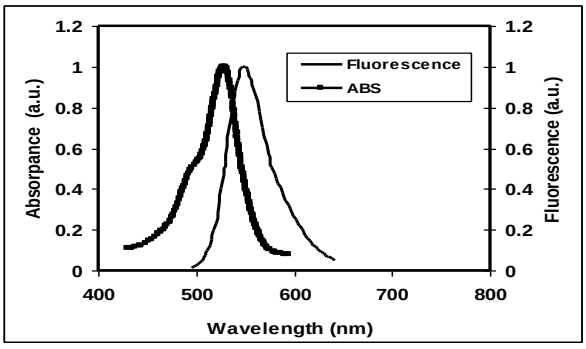

Figure (5) Absorption and fluorescence spectrum of R 6G&R3GO & RB mixture at [3:1:1] ratio.

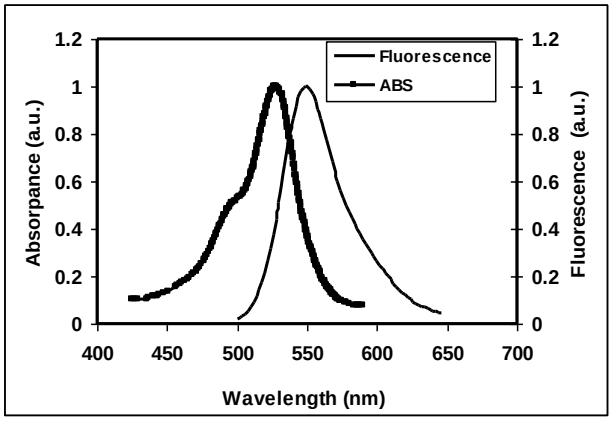

Figure (6) Absorption and fluorescence spectrum of R 6G&R3GO & RB mixture at [4:1:1] ratio.

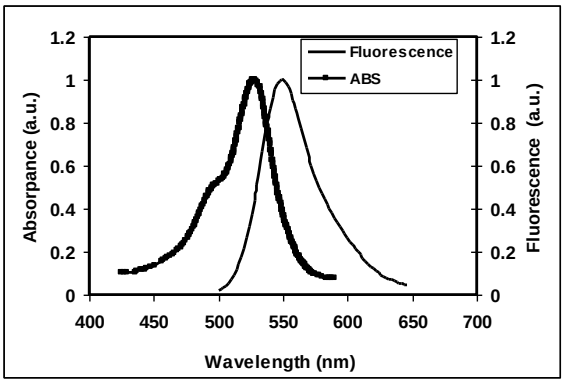

Figure (7) Absorption and fluorescence spectrum of R 6G&R3GO &R B mixture at [1:2:1] ratio.

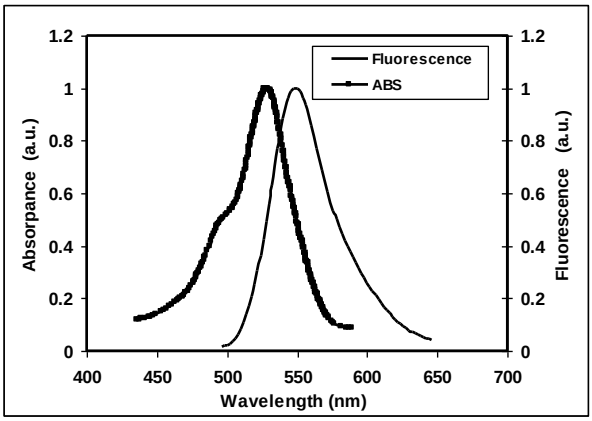

Figure (8) Absorption and fluorescence spectrum of R

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6G&R3GO &R B mixture at [1:3:1] ratio.

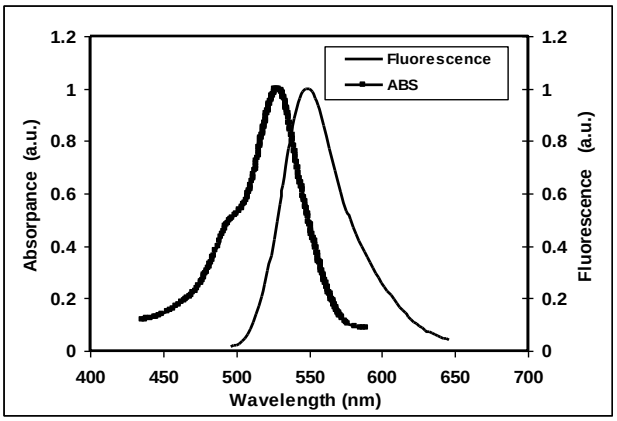

Figure (9) Absorption and fluorescence spectrum of R 6G&R3GO & RB mixture at [1:4:1] ratio.

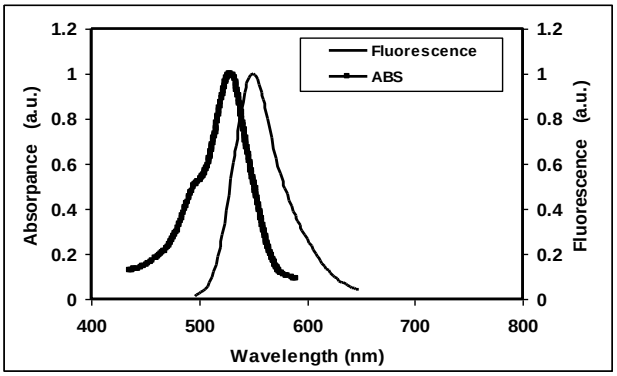

Figure (10) Absorption and fluorescence spectrum of R 6G&R3GO &R B mixture at [1:1:2] ratio.

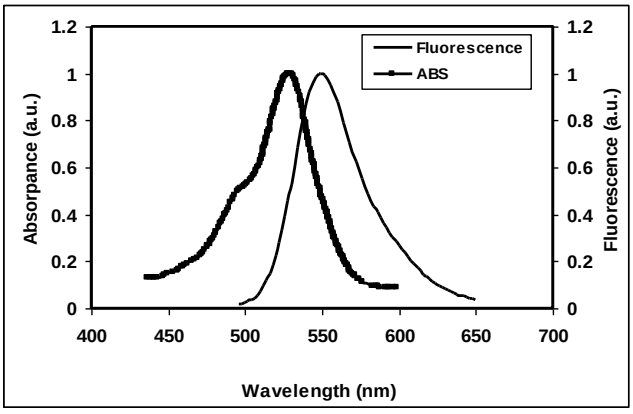

Figure (11) Absorption and fluorescence spectrum of R 6G&R3GO &R B mixture at [1:1:3] ratio.

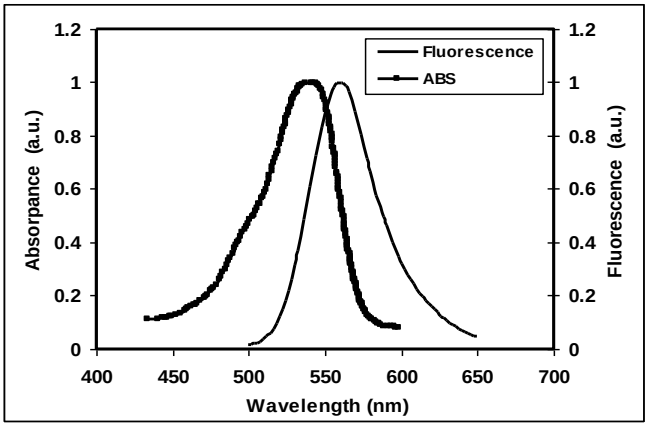

Figure (12) Absorption and fluorescence spectrum of R 6G&R3GO & RB mixture at [1:1:4] ratio.

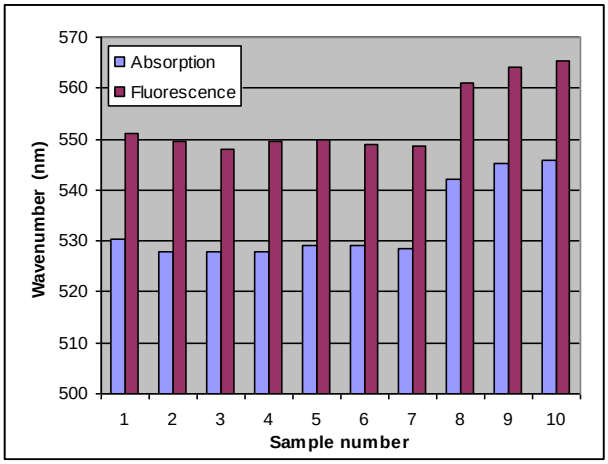

Figure (13) Show the absorption and fluorescence shift for samples.

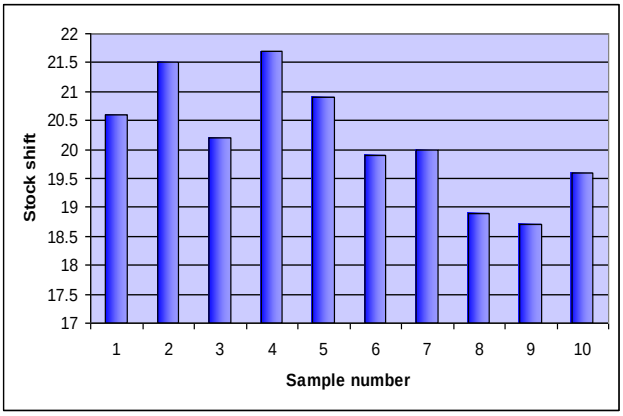

Figure (14) Show the stock shift between fluorescence and absorption of samples.