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ABSTRACT

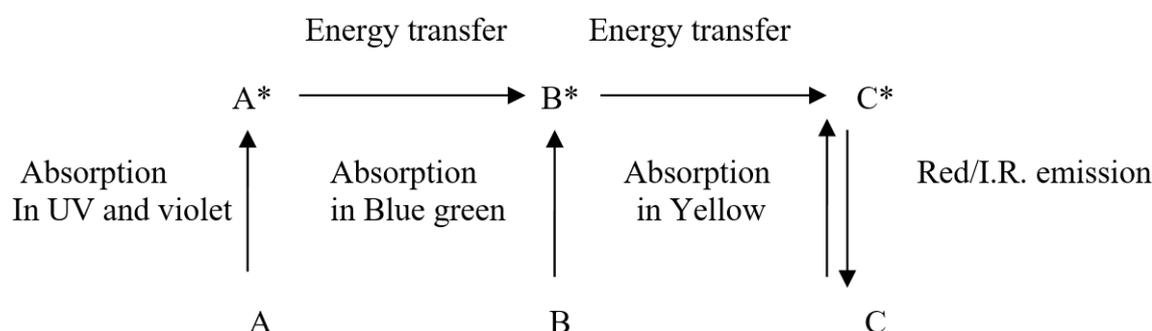
In the present study, investigation of Förster energy transfer and energy migration in dye pair coumarin6-rhodamine6G doped in poly(methylmethacrylate) thin films as well as excitation energy transfer in ternary dye system coumarin102-coumarin6-rhodamine6G doped in poly(methylmethacrylate) is investigated. These two and three dyes doped transparent films can be used as efficient materials in luminescent solar collectors.

Keywords: Energy transfer, energy migration, luminescent solar collectors

INTRODUCTION

Enhancement in the performance of luminescent solar collectors (LSC,s) with multiple dye systems was first reported by Swartz et al.1977(Swartz et al.,1977). The multiple dye-doped polymers are very useful for the transmutation of light radiations as they allow energy transfer over a wide spectral range with higher efficiency. Applications like energy transfer dye laser (Saito et al.,1988,1992; Yang et al., 2005; Raju et al., 1993,1995; Rivero et al., 2014; Sebastian et al., 1980) and luminescent solar collectors employ ternary dye doped polymer systems which better their performance (Bailey et al.,2007; Liu et al., 2015). The excitation of a dye mixture through energy transfer phenomena can provide extended lasing wavelength region with enhanced efficiency. The mechanism of a

ternary dye system can be understood as follows: One of the dyes A, the donor, absorbs at a shorter wavelength for example, the ultraviolet or blue radiation. By means of energy transfer (Forster or migration) to an acceptor dye B the radiation is red shifted and the red-shifted emission which is then transferred to dye C which is more red shifted. The mechanism of energy transfer and absorption can be shown as in *Scheme 1*. In this way, the range of spectral absorption is extended and the emission is red shifted. The main mechanism proposed for such an energy transfer is short and long range energy transfer due to dipole-dipole coupling between the donor and acceptor molecules during the excitation lifetime of the donor (Lin et al., 1973).



Scheme 1

A no. of ternary dye systems like Coumarine 440 + Coumarine 485 + Rhodamine 610 perchlorate (Sharma et al., 2009), Stilbene 420-Coumarine 540-Nile Blue(Sanghi et al., 1997)and 9 amino acridine hydrochloride hydrate-acriflavin-rhodamine B-doped PVA films(Naithani et al., 2011) have already been investigated and documented in literature. Energy transfer study are important because of their applications in luminescent solar collectors(LSC) (Mishra and amishar 2008a). These collectors have been found to be cost effective and possess high efficiency (Mishra and Mishra, 2008a, 2007, 2008b). The aim of these studies is to find appropriate donor acceptor pair to utilize the solar radiations in the UV-visible to actualized the intensity in the infrared region by means of energy transfer. This is achieved by using two or multiple dye doped in thin polymer films used in solar concentrations.

In the present work, for ternary system we chose blue emitting dye coumarin102(donor), to make sure that the blue part of the spectrum is also absorbed and shifted to red emitting dye rhodamine6G(acceptor) through energy transfer with high quantum efficiency, Coumarin6 used as a mediator dye. For this the energy transfer in binary systems C102-C6 and C6-Rh6G have been studied. The energy transfer between C102 and C6 have already been published by K. Singh et al.2018. In the present work, we have studied excitation energy transfer and migration in a new donor-acceptor pair coumarin6-rhadamine6G dyes doped in transparent film of Poly methyl methacrylate (PMMA). All dyes used in the present work are laser dye and have high absorptivity as well as high quantum yield of emission. Therefore, all dyes can be used as LSCs materials. PMMA has been chosen as a host material due to its excellent properties for use in luminescent solar collectors (highly transparent and large refractive index) (Pandey et. al., 1989). One of the primary aims of the study is to find a low cost collectors having highly efficient energy transfer, for the relatively high cost dyes used in the luminescent solar collectors.

2. Experimental Procedures

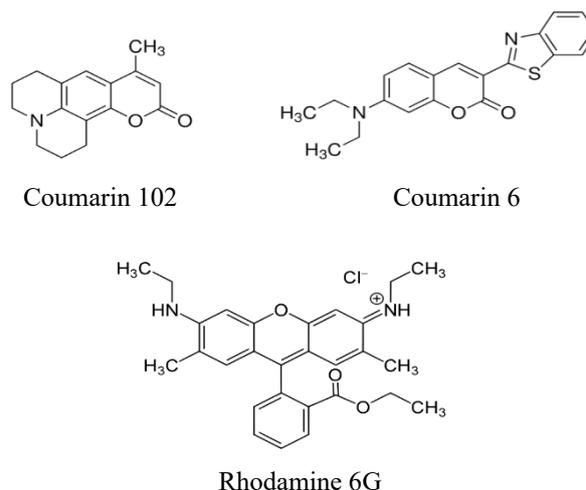
2.1. Materials used

The chemicals used are as follows:

- i. Coumarin102
- ii. Coumarin6

- iii. Rhodamine6G
- iv. Poly(methylmethacrylate)
- v. Dimethylformamide

Were obtained from Sigma Aldrich USA and Hi-media, India and were used without further purification. The solvent (DMF) used in this study is of spectroscopic grade. *Scheme 2* gives the molecular structures of the dyes used under the study.



Scheme 2

2.2. Sample preparation

C6 and Rh6G doped PMMA films were prepared by dissolving the required amount of PMMA in di methyl form amide (DMF) and mixing it with the desire concentration of dyes dissolved in the same solvent at 40°C. The thickness of the films (~0.3mm) was kept constant by using equal weight of PMMA for all the samples. C102-C6-Rh6G doped PMMA films were prepared by same method.

2.3. Experimental setup

Absorption and fluorescence spectra were recorded by using Perkin-Elmer Lambda-35 UV-Visible spectrometer and Perkin-Elmer LS-55 fluorescence spectrometer respectively. The fluorescence spectra were recorded under constant geometric conditions. Fluorescence decay times were recorded using Edinburgh Instrument (EI) FLA-199 time domain single photon counting spectrometer and analyzed by related software as described in ref.(Joshi et al., 2000). A thyratron gated hydrogen lamp was used as excitation source. The excitation and emission wavelengths were taken at 450nm and

530nm respectively for recording the decay. The instrumental /Lamp profile (IRF) was measured at the excitation wavelength using Ludox scatter. Photomultiplier tube (PMT) XP2020x was used as detector. The decay curves were fitted using single exponential fit and Förster fits by judging the χ^2 values, standard deviations and residuals.

RESULTS AND DISCUSSION

3.1. Energy transfer in binary dye system coumarin6-rhodamine6G

3.1.1. Effect of Rhodamine6G concentration on emission intensity of Coumarin6

Absorption and emission spectra of C6 (donor) in PMMA has already been published (K.Singh et

al.,2018) and Rh6G (acceptor) in PMMA is shown in Fig.1 and the position of band maxima are given in Table 1. The maximum absorption wavelength of the dye C6 is around 460nm and the maximum emission of C6 occurs at 515nm (K.Singh et al.,2018). For rhodamine6G the absorption and emission maxima lie at 535nm and 600nm respectively. The absorption and emission spectra of C6 and Rh6G do not show any concentration dependence up to the concentration used under the study and it rules out the possibility of the formation of dimers (or) higher aggregates. No new absorbing species is formed when C6 and Rh6G are mixed together in PMMA matrix which is evident from the fact that the spectra remain unaffected upon change in the concentrations of the dyes.

Table 1. Photo physical parameters for Coumarin6-Rhodamine6G system in PMMA

Donor		Acceptor		$J(\lambda)(M^{-1}cm^3)$	$R_0(\text{Å})$	$J_{OD}(\lambda)(M^{-1}cm^3)$	$R_{OD}(\text{Å})$	(α/β)
λ_{abs}	λ_{em}	λ_{abs}	λ_{em}					
460nm	515nm	535nm	600nm	11.3×10^{-13}	72	1.2×10^{-13}	49.2	0.9

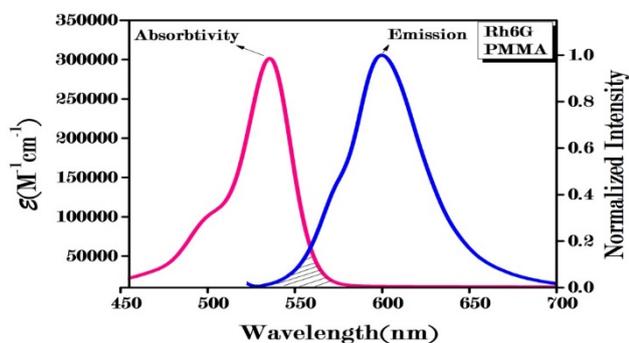


Fig.1. Absorption and emission spectra of rhodamine6G ($1 \times 10^{-4}M$) in PMMA.

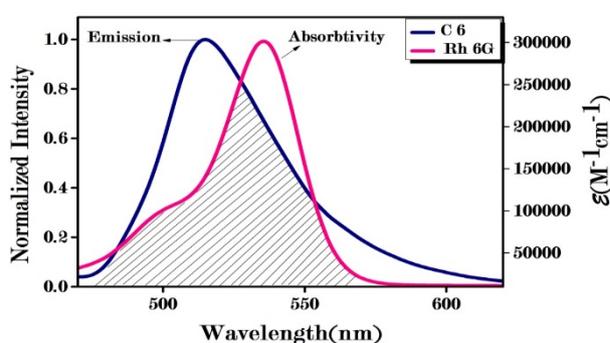


Fig.2. Spectral overlap of the absorption spectrum of rhodamine6G and the emission spectrum of coumarin6 in PMMA.

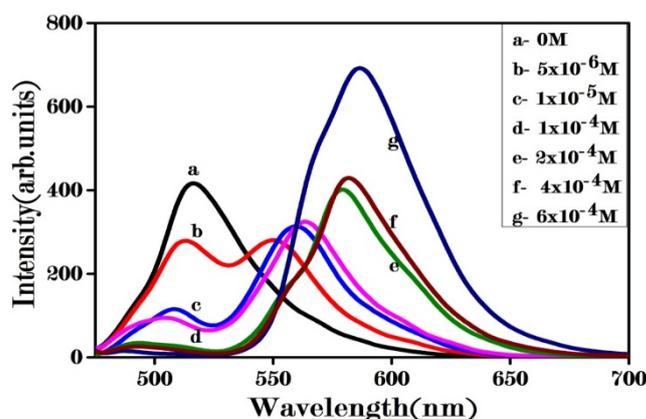


Fig.3. Variation in emission intensity of donor (C6 fixed at $1 \times 10^{-4}M$) on increasing acceptor (Rh6G) concentration (from 0M to $6 \times 10^{-4}M$).

Fig.2 shows the spectral overlap between absorption spectrum of Rh6G and emission spectrum of C6. The overlapping condition is an important factor for an efficient energy transfer from donor to acceptor as confronted according to Förster theory (Förster, 1959). In addition, there is a significant overlap between the absorption and fluorescence spectra of C6(donor) itself as evident from our previous work (Singh et al.,2018) indicating the possibility of donor-donor migration of excitation energy. Therefore, in the present study there are possibly two types of energy transfer viz. long range Förster energy transfer and short range migration. The value of overlap integral $J(\lambda)$ for donor-acceptor system is $11.3 \times 10^{-13} \text{ M}^{-1} \text{ cm}^3$ using,

$J(\lambda) = \int_0^\infty F_D(\lambda) \epsilon_A(\lambda) \lambda^4 d\lambda / \int_0^\infty F_D(\lambda) d\lambda$ and the critical transfer distance R_0 between donor-acceptor is $72(\text{\AA})$ using, $R_{0A} = 9.78 \times 10^3 [\kappa^2 n^4 Q_D J(\lambda)]^{1/6}$ (Förster, 1959) (using measured value of $Q_D = 0.78$ (G.A.Reynolds et al., 1975) and $n = 1.4$ (Pandey et al., 1988)). On the other hand, the values of overlap $J_{DD}(\lambda)$ and critical transfer distance R_{0D} for donor-donor interaction are $1.2 \times 10^{-13} \text{ M}^{-1} \text{ cm}^3$ and $49.2(\text{\AA})$ respectively (Table 1). and the ratio of donor-acceptor and donor-donor interaction parameters (α/β) is 0.9 by using, $\alpha = 1/\tau_D(R_{0A})^6$ and $\beta = 1/\tau_D(R_{0D})^6$ (Huber,1979a,1979b) which suggests a higher dipole-dipole energy transfer rate are listed in Table1.

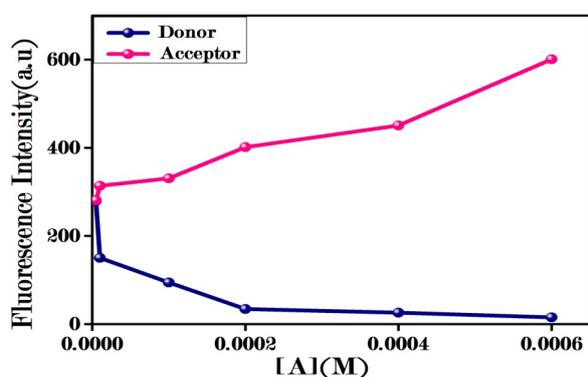


Fig.4. The variation of donor and acceptor fluorescence intensities with acceptor concentration for C6-Rh6G.

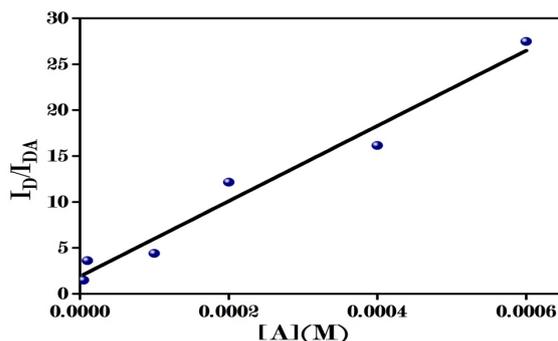


Fig.5. Stern-Volmer plot for C6-Rh6G dye pair in PMMA.

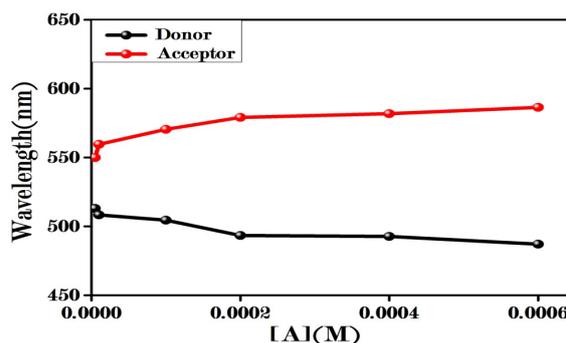


Fig.6. The variation of donor and acceptor emission peak wavelength in C6-Rh6G with acceptor concentration.

The fluorescence spectra of C6 in the presence of different concentrations of Rh6G are shown in Fig.3. In all spectra, the concentration of coumarin6 ($1 \times 10^{-4} \text{ M}$) was kept constant, whereas the concentration of rhodamine6G varied from 0M to $6 \times 10^{-4} \text{ M}$. For all the samples the geometrical conditions were kept strictly indistinguishable. The excitation wavelength for all the samples was kept at 450nm as at this wavelength the absorption by Rh6G is very small. It is evident from these spectra that with the increase in the concentration of Rh6G successive quenching of coumarin6 fluorescence occurs accompanied by successive enhancement in the fluorescence intensity of Rh6G (Fig.4). Since Rh6G is not directly excited at the wavelength of excitation (450nm), the enhancement of Rh6G fluorescence is due to energy transfer from C6. The Stern-Volmer plot found to be linear as shown in Fig.5. A red shift is observed in the Rh6G fluorescence maxima with increase in the acceptor concentration. Due to the spectral overlap between the donor and acceptor fluorescence which recedes with increasing acceptor concentration (Mishra et al., 2006). There is also a probable violet shift in the donor emission possibly due to self-absorption (Fig.6). However, the steady state data qualitatively indicate the existence of

energy transfer. For perceptible understanding time domain analysis is necessary.

3.1.2. Fluorescence Decay Measurements

The fluorescence lifetime of C6 (1×10^{-4} M) (pure donor) is 4.0ns. The decay is single exponential with χ^2 value equals 1.4 and fit is very good as shown in Fig.8. Addition of Rh6G results in deviation from single exponential decay to non-exponential(Fig.9.) and the lifetime of C6 fluorescence decreases (Table 2). The deviation from single exponential becomes

more perceptible with the increase in the Rh6G concentration and χ^2 shows a gradual increase. The decay curves at higher acceptor concentrations fit well into the Förster's equation of energy transfer $I_D = I_0 \exp(-t/\tau_D) \exp[-2\gamma_{DA}(t/\tau_D)^{1/2}]$ (Förster, 1959). The analysis of the experimentally observed decay data can be divided into two categories: (i) low acceptor concentrations and (ii) high acceptor concentrations.

3.1.2.1. At Low Acceptor Concentration

The decay curves for C6 (donor) (1×10^{-4} M) in the presence of low concentrations of Rh6G (upto 1×10^{-4} M) do not significantly deviate from single exponential. The decay parameter obtained from single exponential fit and Förster fit for different combinations of donor-acceptor concentration are given in Table 2. There is a regular increase in the value of γ (reduced concentration) with increase in the acceptor concentration coherently determined on the basis of Förster theory. In order to compare these γ values with theoretical data have been reproduced in Table 3. The values of critical acceptor concentration $[A_{0A}]$, the critical transfer distance R_{0A} and γ_{DA} for all donor-acceptor concentrations have been calculated by using the equations: $\gamma_{DA} = [A_A] / [A_{0A}]$ and $[A_{0A}] = 3000 / 2\pi^{3/2} N R_{0A}^3$ (Förster, 1959). It can be seen that concentration of Rh6G increases, the observed value of the reduced concentration γ_{obs} (experimental value) shows a regular increase. However, it is close to the γ_{DA} (theoretical value) only at higher concentration. Also, at low acceptor concentrations up to 1×10^{-4} M the observed values of critical transfer distance R_{0A} is much greater than the value of critical transfer distance R_0 (72 \AA) obtained from steady-state spectral measurements. Thus at low concentrations of Rh6G fitting of data with Förster's function seems discrepant. This discrepancy is due to the fact that Förster theory assumes low donor and high acceptor

concentration. At low acceptor concentrations the rate of donor-donor migration is prominent and the donor-acceptor transfer rates are comparable only at higher concentrations. Therefore, the role of donor-donor excitation migration becomes significant as suggested by Huber (1979a, 1979b) and LAF (Loring et al., 1984). The modified decay functions according to Huber (1979a, 1979b) and LAF (Loring et al., 1984) are given by equation: $I_D = I_0 \exp[-(t/\tau_D) - 2(\gamma_{DD}/2^{1/2} + \gamma_{DA})(t/\tau_D)^{1/2}]$ and assumes the same form as the Förster's function with γ_{DA} replaced by γ_{cal} ($=\gamma_{DD}/2^{1/2} + \gamma_{DA}$), γ_{DD} is related to the donor-donor interaction and can be calculated by using the relation $\gamma_{DD} = [A_D] / [A_{0D}]$. Values of γ_{cal} are quite in agreement with γ_{obs} and the corresponding values of R_{0A} also given in Table 3. Thus at low acceptor concentrations the theoretical models of LAF and Huber satisfactorily explain the energy migration. The value of γ_{DD} (0.0267) is more than the γ_{DA} values at low acceptor concentrations. It signifies a higher contribution of the migration at low acceptor concentrations.

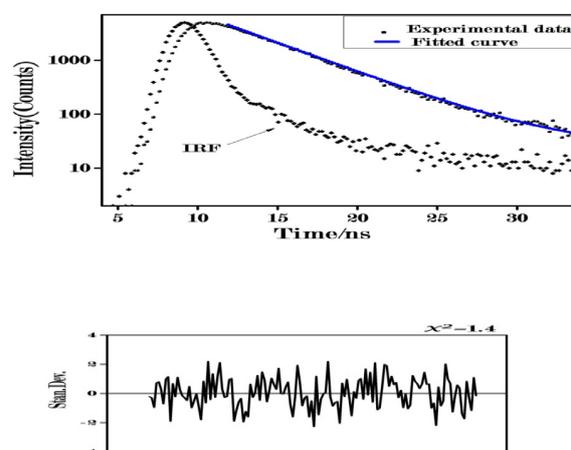
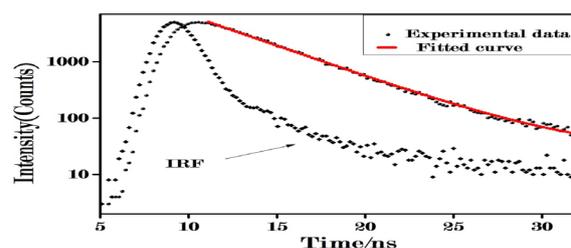


Fig.7. Fluorescence decay curve of C6 (pure donor at 1×10^{-4} M) in thin film of PMMA at 530nm (λ_{exc} : 450nm). Fitted with a single exponential function.



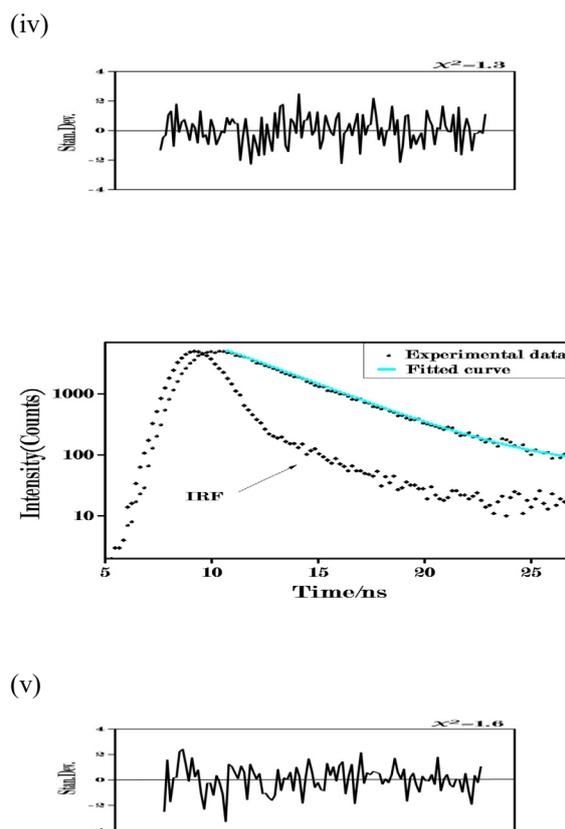
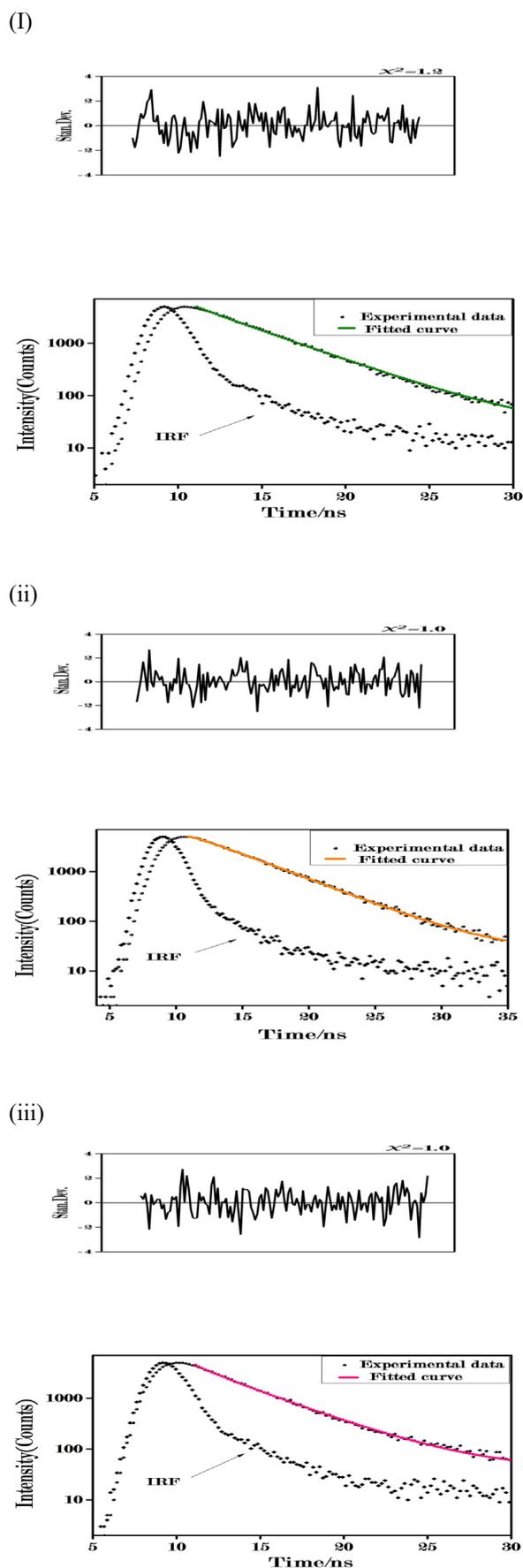


Fig.8. Standard deviations for Förster function fitted decay curves of C6 (donor at $1 \times 10^{-4} \text{M}$) in thin film of PMMA at 530nm (λ_{exc} : 450nm) with varying concentration of Rh6G (acceptor). Rh6G concentrations are (i) $5 \times 10^{-6} \text{M}$, (ii) $1 \times 10^{-5} \text{M}$, (iii) $1 \times 10^{-4} \text{M}$, (iv) $2 \times 10^{-4} \text{M}$, (v) $4 \times 10^{-4} \text{M}$ and (vi) $6 \times 10^{-4} \text{M}$. Plotted are the experimental data (points) and the fitted data (colorful lines). Residuals and χ^2 values are also shown for each donor-acceptor combinations.

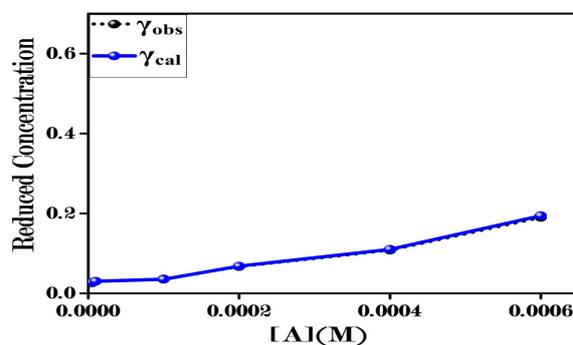


Fig.9. Plot of the observed value (γ_{obs}) and calculated value (γ_{cal}) of the reduced concentration vs. acceptor concentration for C6-Rh6G in PMMA.

Table 2
Experimentally obtained parameters for C6-Rh6G system in PMMA for single exponential and Förster fit (λ_{exc} : 450nm)

[A](M)	Single exponential fit			Förster fit	
	τ (ns)	χ^2	$(\gamma)_{obs}$	τ (ns)	χ^2
0	4.0	1.4	-	4.0 (fixed)	-
5x10 ⁻⁶	3.8	1.3	0.026	„	1.0
1x10 ⁻⁵	3.5	1.3	0.030	„	1.06
1x10 ⁻⁴	3.4	1.9	0.036	„	1.3
2x10 ⁻⁴	3.3	2.9	0.067	„	1.2
4x10 ⁻⁴	3.09	3.5	0.108	„	1.6
6x10 ⁻⁴	2.7	6.4	0.190	„	1.4

Table 3
Experimentally observed and spectroscopically calculated values of various parameters in C6-Rh6G system.

[A](M)	Observed values			Spectroscopic values		
	γ_{obs}	$[A_{0A}](\times 10^{-3}M)$	$R_{0A}(\text{Å})$	γ_{DA}	γ_{DD}	$\gamma_{cal}(=\gamma_{DD}/2^{1/2} + \gamma_{DA})$
5x10 ⁻⁶	0.026	0.03	226.5	0.0008	0.0267	0.027
1x10 ⁻⁵	0.030	0.16	138.9	0.0042	0.0267	0.030
1x10 ⁻⁴	0.036	0.27	117.1	0.0084	0.0267	0.035
2x10 ⁻⁴	0.067	0.74	84.2	0.0420	0.0267	0.068
4x10 ⁻⁴	0.108	0.92	78.4	0.0840	0.0267	0.110
6x10 ⁻⁴	0.190	1.05	75.1	0.1680	0.0267	0.194

3.1.2.2 At High Acceptor Concentrations

As the concentration of Rh6G is increased the deviation of the decay of C6 from exponential behaviour to non-exponential behaviour becomes more prominent. The observed value of the reduced concentration γ_{obs} obtained from Förster fitting increases with increase in the acceptor (Rh6G) concentration. As mentioned before, the decay data fit well with the Förster expression as demonstrated by

good value of the χ^2 . It can be seen in Table3 that the value of critical transfer distance obtained from steady-state spectral measurements (72 Å) match well with the observed values at higher acceptor concentration. This indicates that the occurrence of Förster energy transfer at higher acceptor concentrations in binary system C6-Rh6G. However, a drastic deviation was seen for lower acceptor concentrations, this indicates that at higher acceptor

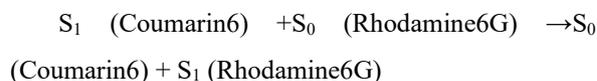
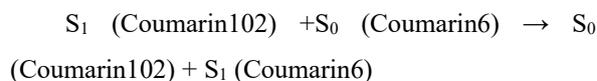
concentrations the Förster mechanism (Förster, 1959) dominates over migration.

Various energy transfer parameter between acriflavin-rhodamineB and acriflavin-malachite green doped in PMMA has been studied earlier (Pandey et al., 1989,1988; Mishra et al.,2006; Tripathy et al., 2006; Mishra et al.,2008). Pandey et al., (1988), (1988) investigated the excitation energy migration and transfer between acriflavin and rhodamine6G doped in PMMA. Tripathi et al., (2006) studied the migration and diffusion modulated excitation energy transfer in a dye pair 7-diethylamino-4-methylcoumarin and 3,3'-dimethyloxycarbocyanine iodide. In various polymers PVA, cellulose acetate and PMMA, the excitation energy transfer between acriflavin and rhodamine6G has also been studied (Mishra et al.,2008). Our results for the C6 to Rh6G donor acceptor system are in agreement to the view that the migration of energy between donors is also an important pathway of energy transfer particularly at low acceptor concentrations. However, at high acceptor concentrations the migration effect is masked by highly efficient Förster dipole-dipole energy transfer between donor and acceptor molecules. Absorption of rhodamine6G extends mainly in the spectral range 470nm-560nm Fig.1. On other hand Coumarin6 absorbs in the spectral range 400nm-470nm. A mixture of coumarin6 and rhodamine6G will enable absorption within the spectral range 400nm-560nm. Energy transfer from coumarin6 to rhodamine6G will increase the intensity of emission of rhodamine6G. As both migration and dipole-dipole mechanisms are responsible for energy transfer, by optimizing both donor as well as acceptor concentrations an efficient energy transfer can be achieved for proper use in LSCs.

3.2. Energy transfer in coumarin102-coumarin6-rhodamine6G ternary system

It is clear from our previous study that in the dye mixtures doped in PMMA, energy transfer from donor to acceptor occurs mainly by two process viz donor-donor excitation migration at low acceptor concentrations and Försters mechanism at high acceptor concentrations. As already observed that two C6 make good pair with C102 for efficient energy transfer and has highly efficient energy transfer rate with Rh6G. Coumarin6 dye is highly suitable to act as

an intermedior dye for ternary dye system. Thus in the present study we have investigated two ternary dye systems doped in PMMA viz



Where S_0 and S_1 are the ground and excited singlet states of the dyes.

Fig.10. shows the variation of the fluorescence spectra of C102-C6-Rh6G doped in PMMA. The concentration of C102 has been kept at $1 \times 10^{-4} \text{M}$ and of C6 at $2 \times 10^{-5} \text{M}$. Concentration of Rh6G has been increased from 0M to $4 \times 10^{-4} \text{M}$. Excitation wavelength for all concentrations has been kept at 360nm. At 0M of Rh6G the emission bands of both C102 and C6 are clearly perceptible.

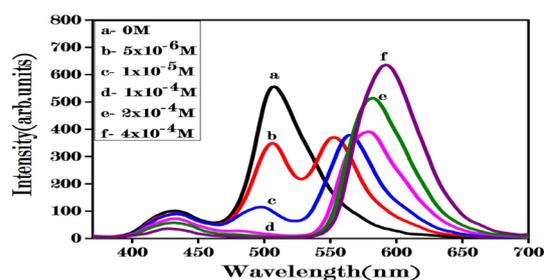


Fig. 10. Fluorescence emission spectra of C102-C6-Rh6G in PMMA. C102 and C6 concentration is fixed at $1 \times 10^{-4} \text{M}$ and $2 \times 10^{-5} \text{M}$ respectively. Rh6G concentration is varied as (a) 0M, (b) $5 \times 10^{-6} \text{M}$, (c) $1 \times 10^{-5} \text{M}$, (d) $1 \times 10^{-4} \text{M}$, (e) $2 \times 10^{-4} \text{M}$ and (f) $4 \times 10^{-4} \text{M}$.

The energy transfer from C102 to C6 and the decrease in intensity of C102 with increasing C6 concentration have already been reported (K. Singh et al., 2018). The C102 emission almost disappears at C6 concentration equal to $6 \times 10^{-4} \text{M}$. This has been shown in Fig.11. At this concentration the intensity of C102 emission decreases by 95% when compared to emission of C102 without the presence of C6. In the similar manner the decreases in the intensity of C6 emission with increasing Rh6G concentration has been investigated in the present study. The excitation wavelength for this study has been kept 450nm. Fig.12 shows the emission intensity of C6-Rh6G at two concentrations of Rh6G viz 0M and $6 \times 10^{-4} \text{M}$ and it is seen that the intensities of C6 decreases by almost

97%.

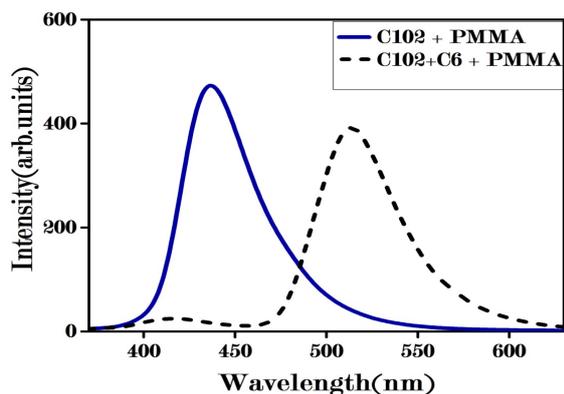


Fig.11. Fluorescence spectra of pure donor C102 ($1 \times 10^{-4}M$, blue line) and fluorescence spectra of C102 ($1 \times 10^{-4}M$) + C6 (acceptor, $6 \times 10^{-4}M$) shown by black dotted line doped in PMMA.

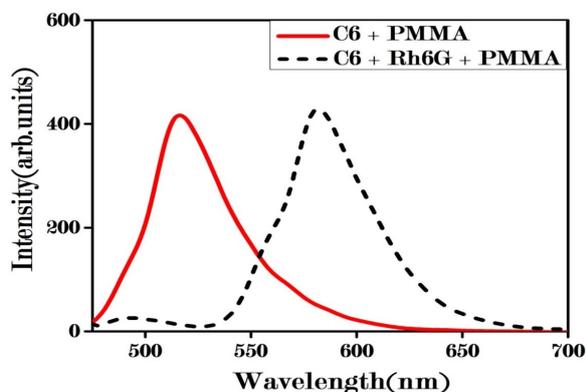


Fig. 12. Fluorescence spectra of pure donor C6 ($1 \times 10^{-4}M$, red line) and fluorescence spectra of C6 ($1 \times 10^{-4}M$) + Rh6G (acceptor, $6 \times 10^{-4}M$) shown by black dotted line doped in PMMA.

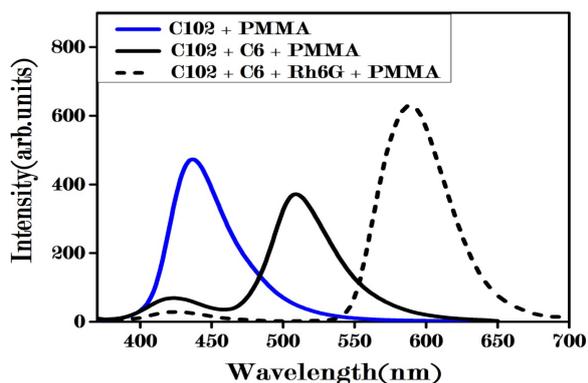


Fig. 13. Fluorescence spectra of pure donor C102 ($1 \times 10^{-4}M$, blue line), C102 + C6 ($1 \times 10^{-4}M + 6 \times 10^{-4}M$) (black line) and C102 + C6 + Rh6G ($1 \times 10^{-4}M + 6 \times 10^{-4}M + 6 \times 10^{-4}M$) (black dotted line), doped in PMMA.

Fig.13 shows the emission spectra C102 ($1 \times 10^{-4}M$), C102 + C6 ($1 \times 10^{-4}M + 6 \times 10^{-4}M$) and C102 + C6

+ Rh6G ($1 \times 10^{-4}M + 6 \times 10^{-4}M + 6 \times 10^{-4}M$) respectively. It is observed that following the process of energy transfer, there is an overall increase in the Rh6G emission while the emission of C102 and C6 emission are almost inhibited.

The other features of the study of energy transfer are shown in Fig.14 and Fig.15. A minor blue shift is observed in fluorescence peak of coumarin102 and coumarin6 and a red shift in the acceptor (rhodamine6G) side are observed in the fluorescence spectra. These shift trends are pictured in Fig.14. The blue shift of the donor emission spectra observed possibly due to self-absorption.

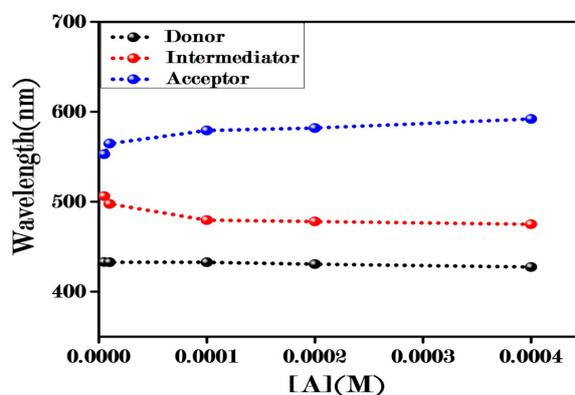


Fig.14. The variation of emission peak wavelength of donor, intermediary and acceptor with acceptor concentration for ternary system C102-C6-Rh6G doped in PMMA.

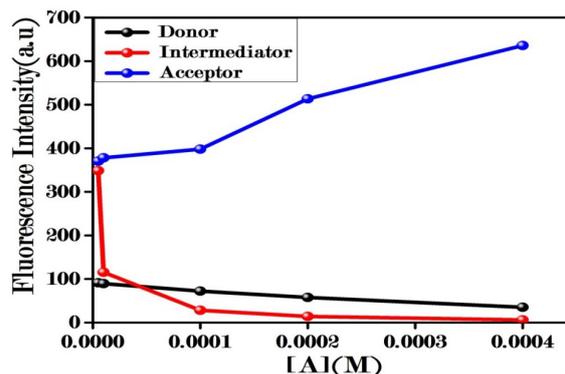


Fig.15. The variation of donor, intermediary and acceptor fluorescence intensity with acceptor concentration for ternary system C102-C6-Rh6G doped in PMMA.

A red shift can be attributed to the spectral overlap between the donor and acceptor fluorescence which reduced with increasing acceptor concentration. With an increase in rhodamine6G concentration, the fluorescence intensity of coumarin102 shows a very

slight decrease (from a value of 100.6a.u to 35.27a.u) while that of coumarin6 shows a regular decreases (from a value of 356.14a.u to 6.04a.u) and fluorescence intensity of rhodamine6G is enhanced successively (from a value of 370.52a.u to 635.72a.u), this indicate a very small energy transfer directly from coumarin102 to rhodamine6G it is evident from Fig.15. Though the concentration of both, coumarin102 and coumarin6 is kept constant, the decrease in intensity of only coumarin6 establishes the path of energy transfer from coumarin102 to coumarin6 and then from coumarin6 to rhodamine6G.

The results clearly show that there is an efficient energy transfer in the ternary dye system C102-C6-Rh6G, the transfer efficiency being considerably high in this system. Coumarin102 absorbs in the region 300-390nm and transfers the energy to coumarin6. Coumarin6 which absorbs in the region (430-480nm) transfers the energy to rhodamine6G which itself absorbs in the region 470-560nm. In this manner the energy absorbed in the region 300-550nm is transferred to enhance the fluorescence intensity in the wavelength region 550-650nm.

Thus, for the ternary systems C102-C6-Rh6G excitation at the wavelength 390 nm is exhibited in the form of emission between 550nm to 650nm. As the absorption by Rh6G at this excitation is weak the enhancement in the intensity of emission of Rh6G is exclusively by excited state energy transfer. In a similar manner the excitation of C6 molecules as a result of absorption in the wavelength region 430 to 500 nm results in the emission in the wavelength region 550 to 650 as a result of energy transfer mechanism. Therefore, the ternary dye system is quite capable for enhancement of intensity of emission of the red emitting dye Rh6G by absorption over a wide range of electromagnetic spectrum which otherwise is limited to a narrow spectral range. The wavelength of emission can be further extended to longer wavelength with the help a quaternary system by adding a dye which is capable to absorb in the wavelength region 550 -650nm corresponding to Rh6G emission and has higher efficiency of energy transfer. The study, however, is not possible in the present investigation because the fluorimeter available with us does not have the facility of detecting the

infrared emission.

CONCLUSION

In the polymer matrix PMMA, at higher acceptor concentration with respect to the donor concentration, direct energy transfer can be explained on the basis of the Forster (1959) theory of fluorescence resonance energy transfer. At low acceptor concentrations with respect to the donor concentration, excitation migration among donor molecules influence the transfer kinetics, and the results are satisfactorily explained on the basis of Theories given by Huber, (1979a,1979b) and LAF (Loring et al.,1984). However, there is an efficient energy transfer from coumarin6 to rhodamine6G at higher acceptor concentration and the pair may be well suited for use in LSCs. The use of multiple dyes connected to a FRET network best solves the issue of improving the wavelength range of absorption of LSCs. Our results show a highly efficient FRET network, composed of C102, C6 and Rh6g dyes as suitable LSC materials, which enables the absorption of the blue wavelength region (300-550) nm and emission in the red region (550-650) nm. Further the suitability of each dye in this cascade is shown by transfer efficiencies besides having high quantum yield and small self-absorption. Thus the ternary systems prove to be very efficient FRET pair and besides being suitable for use in LSCs, can be put to various other uses such as, optical LEDs, optical storage materials and solid state energy transfer dye lasers etc.

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