

Kinetic and Mechanistic features of 6-Chloro-3-hydroxyflavone in Dye sensitized Reaction: Photorearrangement or Photooxidation

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Abstract: In order to understand the kinetics and mechanistic paths adopted, we have been synthesized a versatile novel fluorescent probe 6-Chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (6-CHTF) linked via smaller sized five-membered heterocyclic thienyl moiety at 2nd position. The photolysis reaction of both substrate (4.14×10^{-5} M) and dye sensitizers has been performed through a irradiation source, a medium pressure mercury lamp, additionally placing a filter in front of the lamp for selective excitation wavelength in certain solvent such as acetonitrile. An analysis of the absorption and emission spectra of these molecules upon irradiation explains their product formation, both species rearranged into 6-Chloro-3-hydroxy-3-(2'-thienyl)-indan-1,2-dione, different from photoreaction of the parent compound 3-Hydroxyflavone was further confirmed with IR, PMR and coupling it with *o*-phenylenediamine. Reaction mechanism involved was critically monitored the absorption and emission spectroscopy assay of the samples for assuming a reaction path followed via phototautomer formed through collision between ³[RB]* and triplet state of tautomeric form of 6-CHTF, a mechanism similar to that suggested for the photoreaction of the parent compound.

Keywords: Photorearrangement; Photolysis; Excited-state intramolecular proton transfer; Quantum yield.

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I. Introduction

Nowadays, exogenic antioxidants, widely distributed in the human diet daily, are essential ingredients help to reduce the harmful effects of the oxidative stress. These antioxidants compounds are natural probes exists in the plant kingdom; flavonoids, tocopherols, tocotrienols, stilbenes, phenolic acids and alcohols, etc. Flavones and its derivatives are well known fluorophores which mainly possess many favourable optical properties; easily synthesized methods, reasonable quantum yields and its stability toward light [1-4]. The interesting feature of 3-hydroxyflavone is excited state intra-molecular proton transfer reaction, from its hydroxyl to its carbonyl group [5]. The ESIPT phenomenon was studied in detail under both natural and synthetic derivatives of flavone compound [6]. The two different excited emission bands originated, usually referred as the normal (N*) excited molecule and the other phototautomeric (PT*) states. Numerous experiments have explained the behaviour of 3-hydroxy flavones, the wavelength and intensity of these emissive states are sensitive to the local environment. A new mechanism was proposed by observing the absorption spectra of photoinduced reactions, a bathochromic or hypsochromic shift noticed through strengthening or weakening the hydrogen-bond of the excited states [7].

Photochemistry of flavone molecules plays important role by exhibiting the intense absorption band in the ultra violet region of the electromagnetic spectrum, this factor helps them in screening or protecting the UV sensitive molecules present in plants. Different authors explore the possible mechanism adopted for the formation of photoproduct through many photochemical reactions. The reaction route proposed in the literature mainly for direct excitation of such flavones and some derivatives possess *o*-benzoyl salicylic acid and carbon monoxide as the main products [8] in photooxidation reactions. The photosensitized oxidation of 3HF compound was also carried out, the reaction mechanism route involving a hydroperoxide intermediate produced by singlet oxygen attack to the double bond of ring C, or an endoperoxide intermediate produced by [2+2] cycloaddition of the singlet oxygen to the double bond of the same ring and splitting of the carbon monoxide [9-10]. In another vision of mechanism suggested by Chou *et al.*, the endoperoxide intermediate directly formed from the 3HF. He pointed out that the cycloaddition of the phototautomer 3HF may lead to a tautomeric epoxy intermediate preceding the arrangement into the diketone unlikely [8]. Recently, Protti and his coworkers studied that the hydrogen bond donor solvents increased the reaction rate [11].

An extension of the previous studies, the aim of the present investigation is to clarify the intermediate involved in the dye sensitized photoreactions of 3HF and the possible photoproduct formed through this reaction is also explored in the present paper. We have examined the above studies on 6-Chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (6-CHTF) flavone moiety. In this compound, the smaller size of the five-

membered heterocyclic thienyl analogue (electron rich substituent) at 2nd position of the chromone moiety could allow easy rotation of this moiety and its acquisition of the planar conformation w.r.t. the chrome molecule.

II. Experimental

Materials and Methods:

The synthesis and characterization of studied compound 6-Chloro-3-hydroxy-2-(2'-thienyl)-4-oxo-4H-1-benzopyran (**6-CHTF**) was elaborated in the *ESI*. Rose bengal (RB), Methylene blue (MB) and Eosin yellow (EY) which were purchased by S.D. Fine and Sigma chemicals Co. India and used without further purification. Solvents used in all the experiments are of spectroscopic grade and purchased from Aldrich Chemical Co. India and used as received. In all experiments doubly distilled water was used.

The UV-Visible absorption spectra of all the samples were monitored by a double beam spectrophotometer (Shimadzu, Pharmaspec1700). The fluorescence spectra were recorded with spectrofluorimeter (Shimadzu, RF5301PC, Japan). All spectral measurements were carried out at room temperature (298K).

Synthesis of 6-CHTF:

In this paper, the synthesis of **6-CHTF** has been described in detail. The intermediates of **6-CHTF** can be prepared by following literature procedure [12]. **6-CHTF** was prepared by esterification of p-Chlorophenol with acetic anhydride in addition of conc. H₂SO₄ to produce p-chlorophenylacetate. Further it was heated at 120 °C in an oil bath with anhydrous AlCl₃ to produce 5-Chloro-2-hydroxyacetophenone. Alkaline condensation of thiophene-2-carboxaldehyde with 5-Chloro-2-hydroxyacetophenone was carried out in the presence of NaOH and subsequent oxidative hetero-cyclization of obtained chalcone with hydrogen peroxide. Light yellow crystals of **6-CHTF** were recrystallized twice from CH₃OH: CHCl₃ to give homogenous product according to TLC, ¹H NMR and IR criteria with m.p. 200-202 °C. ¹H NMR data, CDCl₃: δ 7.15-7.69 (m, 6H, Ar), δ 3.61 (s, OH exchangeable with D₂O); IR (KBr, cm⁻¹): 3569 (OH), 2935 (CH Ar), 1640 (C=O).

Sample Preparation:

To avoid any discrepancy in photochemical reactions, usually freshly prepared solutions were used. However, for some compounds concentrated stock solutions were prepared, where it was found that the solution is stable for many days and placed it in dark. Absorbance and fluorescence impurities of such stock solutions were confirmed with UV/VIS absorption and fluorescence spectrophotometer. All experiments were performed with low concentration of solutions (< 1.5 × 10⁻⁵M) to avoid primary or secondary inter filter effects. Sample concentrations of ~10⁻⁵M for absorption and ~10⁻⁶M for fluorescence were employed.

Photolysis assembly for photochemical reactions:

Photosensitized reactions were carried out to investigate the role of singlet oxygen in photo-oxidation reactions. For this, a major consideration was emphasised on the maximum overlapping between the emission and the absorption spectra of the source of irradiation and the compound/sensitizer absorbing the radiation, respectively.

Some organic dyes such as rose bengal, eosin-blue or yellow, and methylene blue, have been choose as widely used effective sensitizers, as these organic dyes possess appropriate energies of triplet states to sensitize oxygen especially (**Table 1**). Methylene blue, a phenothiazinium dye exhibit intense absorbance in the visible region between a range of 550-700 nm, and possess high quantum yield, Φ_A = 0.52 [13]. Rose bengal and eosin, a xanthene dye; exhibit strong absorption bands in the green area of the visible spectrum (480-550 nm) and produce singlet oxygen with significant yields, Φ_A = 0.76 and have high triplet state energy, E_T = 32.0 kcal [13]. In xanthene skeleton, the position of peak maximum (λ_{max}) showed a bathochromic shift as the number and atomic mass of the halogen substituent increased. Likewise, the existence of heavier halogens groups in the dye skelton, also enhance the yield of intersystem crossing (RB_{ISC} = 0.98, MB_{ISC} = 0.50 and EY_{ISC} = 0.30) to the triplet state, E_T of the dye, which is an important criterion for a photosensitizer. Due to this reason, tetra-iodo and tetra-bromo xanthene derivatives, such as rose bengal and eosin yellow, generally more efficient photosensitizes than other halogenated derivatives of organic dyes (**Fig. 1**).

In the photolysis experiments, 3.5 mL solution of **6-CHTF** in CH₃CN were irradiated along with the sensitizer RB Abs₅₅₀ [5.5 × 10⁻⁵ M], MB Abs₆₄₀ [2.0 × 10⁻⁵ M] and EY [6.94 × 10⁻⁵ M] in air-tight condition, exposed with radiation source of high pressure mercury lamp (125 W, Philips India, **6-CHTF** does not have any absorption beyond 400 nm) using 1cm absorption cell in the photolyzer. Therefore, light absorbed by the sensitizer only, a light-green coloured glass filter cut off at λ > 470 nm was placed between the lamp and the photolysis cell for all experiments. The photon flux incident on the sample was determined by chemical actinometer, *via* potassium-ferrioxalate [14] and Benzophenone-benzhydrol actinometer [15-16].

III. Result and Discussion

Photosensitized reactions are the straight forward way to elucidate the physical processes like energy degradation and energy transfer etc. and allied aspects. In the present study, we investigate the comparative photosensitized study of **6-CHTF** with various organic dyes. Primarily, Electronic absorption spectra of **6-CHTF** along with rose bengal which generate approximate 75% of $O_2 (^1\Delta_g)$ was studied in CH_3CN as solvent, and later on also employed on two other sensitizer, methylene blue and eosin yellow. The solvent CH_3CN was chosen for the experiments owing to its double characteristic of being transparent in the region of 234nm and its capability to easily dissolve in both substrate and the sensitizer. Upon incorporation of rose bengal, a long-wavelength absorption band having $\lambda_{max} \sim 550nm$ with a shoulder from 500-520nm was monitored and also in other dye sensitized reactions the concentration of dye has been adjusted so that it will absorb the entire incident light.

The excitation absorption spectra of 3.5 mL reaction mixture of **6-CHTF** ($4.14 \times 10^{-5} M$) with RB ($5.50 \times 10^{-5} M$) in CH_3CN as solvent were recorded at various times of irradiation (**Fig. 2a**). The UV-Visible absorption spectra demonstrated that the absorbance around the main absorption band of the substrate continuously decreased from 1.2 to 0.2 while on the other side there is no change occurs at λ_{max} of sensitizer. Moreover, two isobestic points at 247 nm and 264 nm was also examined throughout the irradiation. However, these two isobestic points shows proportionate increase and decrease in the concentrations of the product and the reactant which indicates the formation of single product only. It also reveals the existence of equilibrium, presumably between the reactant and the product. On this basis, and considering the decrease around λ_{max} of **6-CHTF**, it was concluded that the substrate was completely sensitized by the sensitizer, rose Bengal and photo-rearranged product was confirmed through the excited state(s) of sensitizer. Furthermore for comparison, this approach was successfully applied on other sensitizers also under identical experimental conditions. The photosensitization of **6-CHTF** ($4.14 \times 10^{-5} M$) with MB ($2.0 \times 10^{-5} M$), and EY ($6.94 \times 10^{-5} M$) continuously reduced upon irradiation in CH_3CN solvent. Like in the case of rose Bengal as sensitizer, similar behaviour (**Fig 2b & Fig 2c**), continuously disappearance of substrate (at λ_{max}) in the UV-Visible absorption spectra were monitored by changing the dye-sensitizer. The studied compound demonstrates the expected behaviour with respect to the exciplex as intermediate for product formation; photorearrangement takes place resulting into 6-Chloro-3-hydroxy-3-(2'-thienyl)-1,2-indandione in deaerated solution.

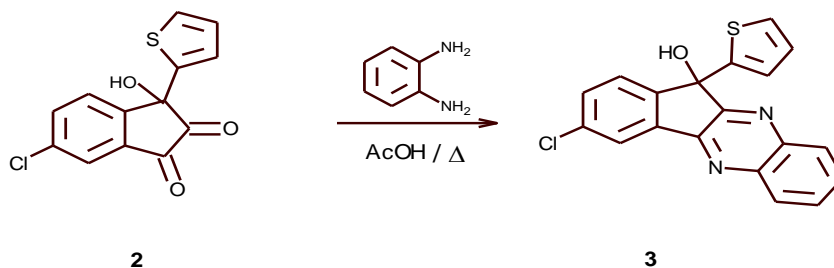
Product of photolysis:

A large quantity of the product was required for measuring the 1H NMR, IR and for coupling with *o*-phenylenediamine. It was obtained then by bulk photolysis of **6-CHTF** solutions ($4 \times 10^{-3}M$) in various lots, each of 50 mL using cyclohexane as solvent were carried in a vessel for predetermined optimum period of 20 hours each, using the same band-pass filter and high pressure mercury lamp, achieving a $\sim 70\%$ conversion. The product was isolated at the end of photolysis; solvent was distilled off with a rotary evaporator under reduced pressure leaving behind a gummy mass. This mass was crystallized from benzene to obtain light steel grey needles m.p. 163-165°C.

The 1H NMR spectrum of product is consistent with the 1,2-indandione. The position of the doublet δ 8.07 ($J = 2.8 Hz$) was assignable to H7 proton, a *dd* centered at δ 7.67 ($J = 4.8 \& 3.5 Hz$) could be arising from H-5', A one proton *dd* restoring at δ 7.50 ($J = 2.8 \& 9.0 Hz$) was described to H-5, A doublet having coupling constant 9.0 Hz at δ 7.21 was due to H-4. Finally, a broad resonating signal at δ 3.60 could be resulting only due to -OH proton. Also conformation of the exchangeable proton (-OH) in this spectrum was determined from the D_2O experiment, where signal due to -OH at δ 3.60 disappeared completely in the spectrum.

IR spectra of the photoproduct showed an intense absorption band at $3479 cm^{-1}$, thus showing the appearance of hydroxyl group. Moreover, the product also showed two intense absorption bands at $1733 cm^{-1}$ and $1682 cm^{-1}$ in the carbonyl region. It concluded that photoproduct possess two carbonyl groups in its structure.

Finally, the structure of photoproduct was confirmed by coupling it with *o*-phenylenediamine in the presence of AcOH, as following;



The IR spectrum of the cycloadduct **3** does not display any absorption in the carbonyl region ($1600\text{--}1750\text{ cm}^{-1}$) showing that both the carbonyl groups of the photoproduct **2** have undergone transformation during the cycloadduct formation. The formation of this cycloadduct also suggests the presence of 1,2-dicarbonyl functionality in its precursor **2**.

Kinetic analysis and Reaction mechanism:

The reaction route of the photosensitized reactions will be proceed through the electronically singlet excited state of the sensitizer; S_n , which is formed by absorbing the sufficient amount of incident radiation, particularly that of the visible light. Relaxation of the normal excited singlet state, S_n of the photosensitizer yielding the lowest excited singlet state of the sensitizer S_1 , whereas on the other hand, intersystem crossing generates the triplet state, T_1 of the sensitizer. The initial step of the substrate **6-CHTF**, is the $S_0 \rightarrow S_1$ excitation of the normal form of **6-CHTF**, followed *via* excited-state intramolecular proton transfer process, ESIPT. Moreover, the ESIPT process is therefore more likely to adopt a low barrier transition state, TS0; resulting lower energy phototautomeric form, S_1 state. Hence, the triplet tautomeric state of **6-CHTF**, ${}^3\text{PT}^*$, was formed through an $S_1 \rightarrow T_n$ inter-system crossing. These results well supported the literature data explained by Zoltan Szakacs *et. al* [17-18].

In photosensitized reaction, an alternative mechanism was proposed *via* transferring energy by collision between ${}^3[\text{D}]^*$ and triplet state of normal form of **6-CHTF**, exciplex as intermediate, which was kinetically accessible. To more closely examine the possible and different paths adopted by product in photosensitized reactions through exciplex intermediate quenching effect, relative reaction rate (RRR) and fluorescence spectroscopy have been proposed. In absorption spectra, the inhibitor effect of sensitizer owing to the presence of **6-CHTF** in concentration of $3.45 \times 10^{-5}\text{ M}$, employing Rose Bengal as a dye-sensitizer was checked. Although high concentration of the flavonoid has been tested, this eliminates the effect of any significant ground state complexation. Another attempt was performed on the fluorescence spectrophotometer under identical conditions (**Fig. 3a**), small concentration of rose bengal ($6.29 \times 10^{-5}\text{ M}$) and **6-CHTF** ($3.45 \times 10^{-5}\text{ M}$) was used for testing, it clearly shows that there is no effect of **6-CHTF** ($\Phi_{em} \sim 0.76$, [19] either on the wavelength or on the yield of emission from ${}^1[\text{RB}]^*$; even, sensitizer also does not affect the fluorescence spectra of substrate (**Fig. 3b**). On this basis and consideration, results clearly indicate the possibility of no exciplexation involved, between ${}^1[\text{RB}]^*$ and ground state of **6-CHTF**.

Next the dependence of RRR on the intensities of absorbed light was interpreted from which information about the involvement of exciplex in the mechanism of the photosensitized reaction can be obtained. It was monitored by varying the light intensities through changing the size of the window and by changing the distance between the cell and the lamp during the photolysis, using RB ($6.29 \times 10^{-5}\text{ M}$) and **6-CHTF** ($3.45 \times 10^{-5}\text{ M}$) in CH_3CN as solvent. Whether exciplex is involved or not, 2nd order dependence of RRR on the concentration of **6-CHTF** was monitored, data better fits in the 2nd order and all the plots are linear as shown in **Fig.4**. Moreover, the rate constants as determined from such second order plots for various intensities of absorbed light, are proportional to the square of intensities of absorbed light (I_a^2) as shown in **Fig.5** rather than I_a . RRR for the different solvents/solvent mixtures where 1,2-dione is formed was also exhibited. RRR as obtained from the slopes of 2nd order plots are smallest in acetonitrile, a non hydroxylic solvent, whereas RRR increases with increasing proportions of IPA in acetonitrile upto $\sim 50\%$ mixture (v/v) beyond which it decreases. IPA is not only a hydroxylic solvent but also has an easily donate proton and therefore, the effect is composite of these parameters. Similar observations for the dependence of fluorescence of 9,10-dicyanoanthracene (DCA) on the incident light intensity was available in the literature [20], suggesting yields of delayed molecular and excimer fluorescence are proportional to $[{}^3\text{DCA}]_0^2$, and hence to the square of the exciting light intensity, I_0^2 . According to W.E. Brewer *et al.*, the rearrangement reaction proceeds through the triplet state of the normal form of the 3-Hydroxyflavone molecule [21]. If exciplex intermediate is operating in our mechanism, then either some low lying triplet state of normal form of **6-CHTF** exists, whose energy is lower than that of $[{}^3(\text{RB}^{2-})^*]$ or triplet state of tautomeric form of **6-CHTF** may have lower energy than $[{}^3(\text{RB}^{2-})^*]$. Finally based on the above observation; I_a^2 is linear, the possibility of triplet-triplet energy transfer between $[{}^3(\text{RB}^{2-})^*]$ to generate tautomeric form of **6-CHTF** will indicates involvement of exciplex somewhere in the mechanism route of the photosensitized reactions. Even an intermediate with different structure was described by Zoltan Szakacs *et. al* this point can not be neglected here [18]. Here, our study has been extended to methylene blue and eosin yellow also, the photolysis of which expected to resulted in the same product as that of the rose Bengal, a xanthene dye but these have not been discussed in detail at present time.

IV. Conclusion

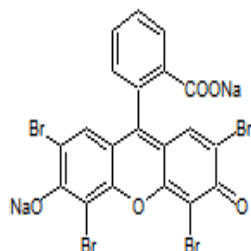
The mechanism of photosensitized reaction of **6-CHTF** with rose Bengal as dye-sensitizer upon rearrangement leading to 1,2-indandione derivative, has been investigate by computing it from the 2nd order dependence of relative reaction rate. The data suggested that intermediate involved in the mechanism route

proceed by the opening of pyrone ring moiety, exciplex formed between [$^3(\text{RB}^2)^*$] and tautomeric form of **6-CHTF** which is then transferred into the final product, 1,2-indanedione through triplet-triplet energy transfer reaction.

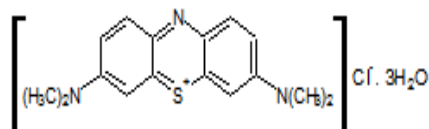
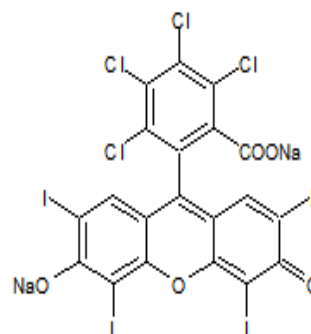
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I- Eosin Yellow (EY)



III- Rose Bengal (RB)



II-Methylene Blue (MB)

Fig. 1: Some common organic photosensitizers.

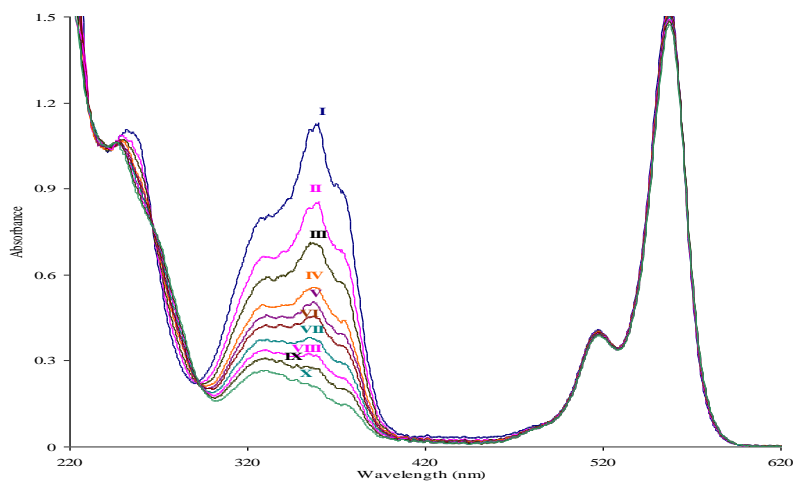


Fig. 2a: Variation of absorption spectra of solution of **6-CHTF** (4.14×10^{-5} M) with Rose bengal as sensitizer, (5.50×10^{-5} M) upon irradiation with visible light > 500 for 0 to 4.0 minutes of photolysis in CH_3CN .

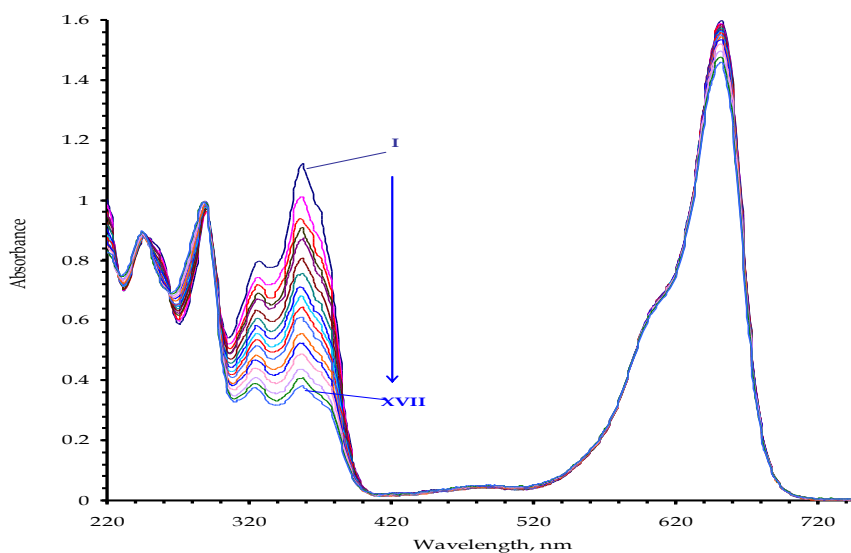


Fig. 2b: Variation of absorption spectra of solution of **6-CHTF** (4.14×10^{-5} M) with MB as sensitizer (2.0×10^{-5} M) upon irradiation with visible light > 500 for 0.0 to 60.0 minutes of photolysis in CH_3CN .

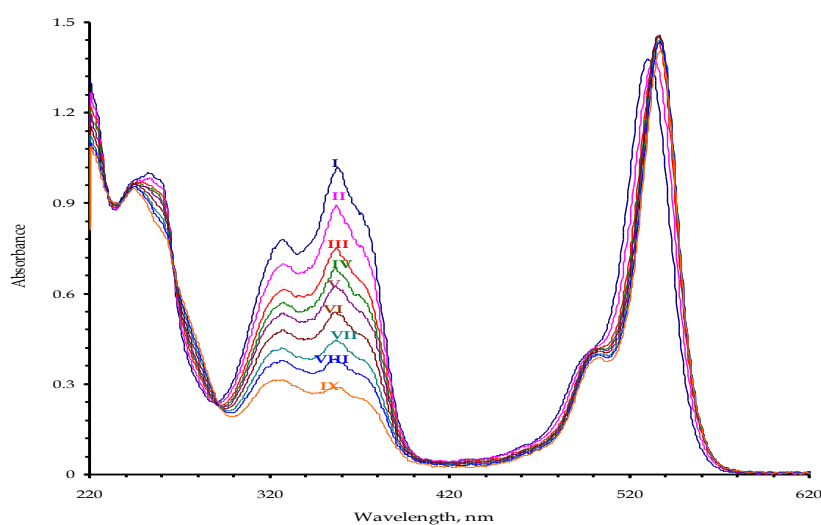


Fig. 2c: Variation of absorption spectra of solution of **6-CHTF** (3.45×10^{-5} M) with EY as sensitizer (6.94×10^{-5} M) upon irradiation with visible light > 500 for 0 to 9.0 minutes of photolysis in CH_3CN .

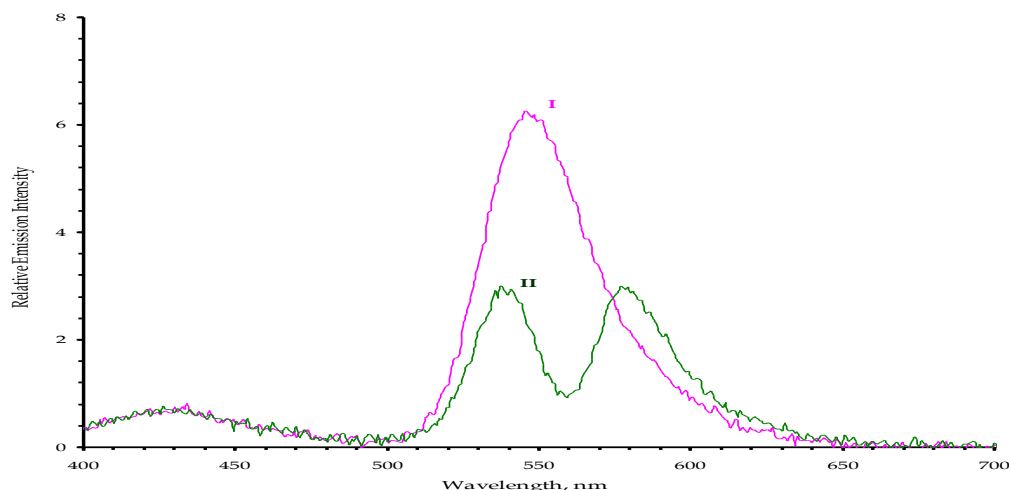


Fig. 3a: Fluorescence spectra showed the effect of quenching by **6-CHTF** ($3.45 \times 10^{-5} \text{M}$) on the RB ($6.29 \times 10^{-5} \text{M}$). **I** and **II** are for **6-CHTF** alone and RB with **6-CHTF** solutions in CH_3CN as solvent. $\lambda_{\text{Exc}}=359.0 \text{ nm}$.

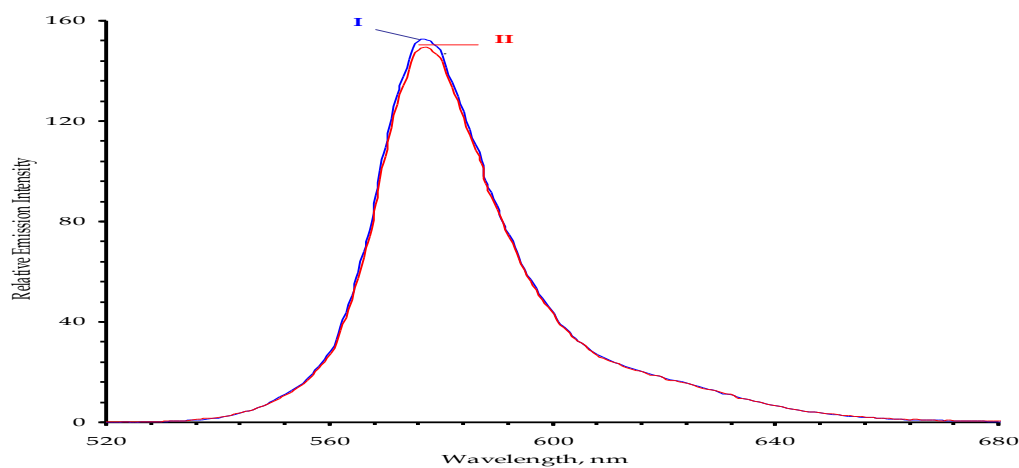


Fig. 3b: Effect of quenching by **6-CHTF** ($3.45 \times 10^{-5} \text{M}$) on the fluorescence spectra of RB. **I** and **II** are for alone RB ($6.29 \times 10^{-5} \text{M}$) and RB with **6-CHTF** solutions in CH_3CN as solvent. $\lambda_{\text{Exc}}=578.0 \text{ nm}$.

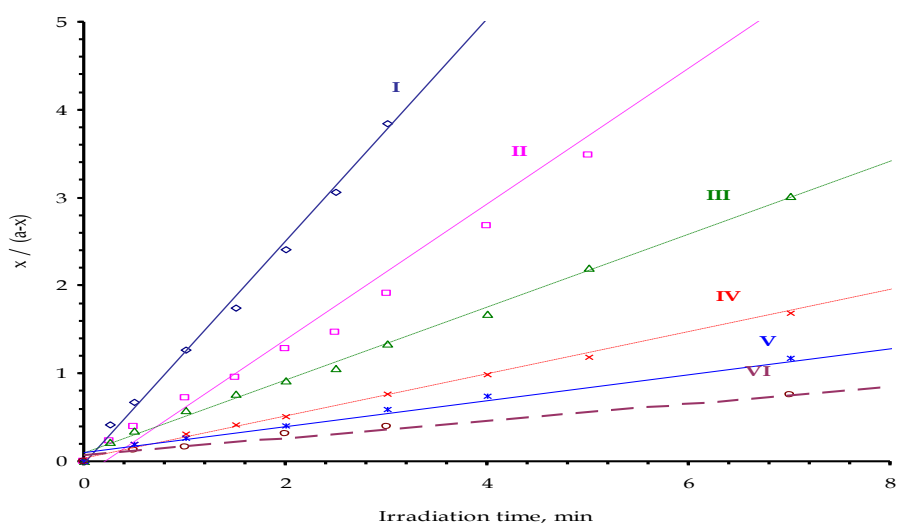


Fig. 4: Plot of 2nd order measured at different light intensities using high pressure mercury lamp (125W) in CH_3CN as solvent, **I–VI** are for 6.25×10^{-7} , 4.75×10^{-7} , 3.50×10^{-7} , 2.60×10^{-7} , 1.75×10^{-7} and 0.60×10^{-7} Einstein/cell/minute.

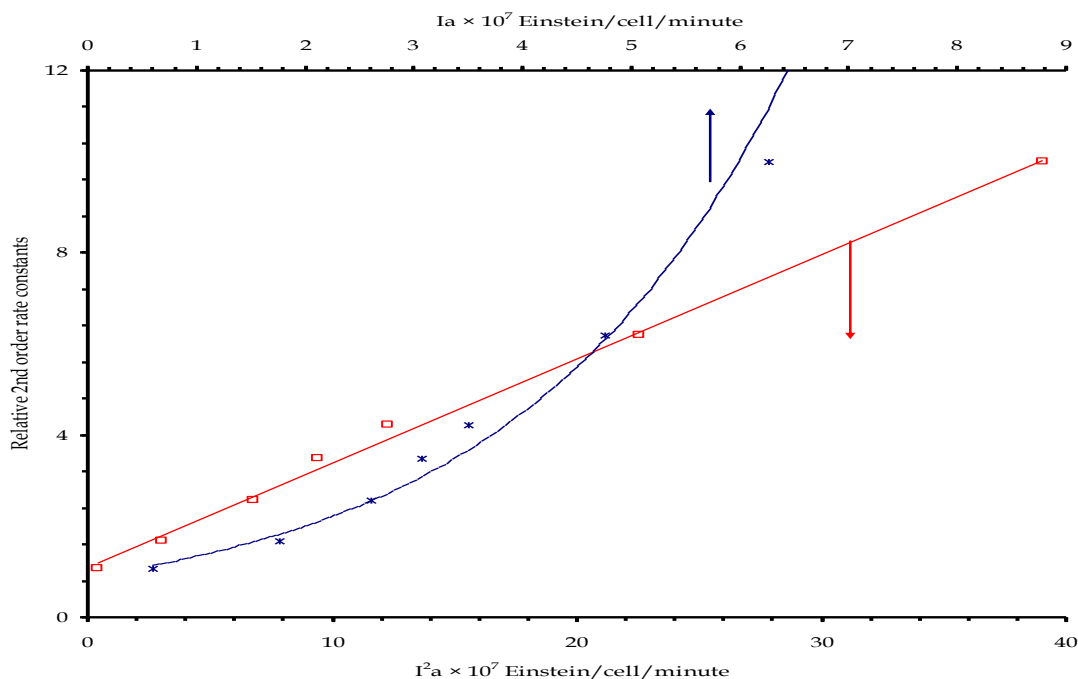


Fig. 5: Plot representing RRR against I_a and I_a^2 using RB sensitizer (6.29×10^{-5} M) and **6-CHTF** (3.45×10^{-5} M) in CH_3CN solvent.

Table 1: Organic dyes with their photo-physical properties.

Parameters	RB	MB	EY	3MF
$^1E_{0-0}^a$ (kcal mol ⁻¹)	50.7	40.8	53.6	73.0 ^b , 74.0 ^d
$^3E_{0-0}^a$ (kcal mol ⁻¹)	39.7	35.2	43.1	0.03 ^b < 0.01 ^d
ISC	0.98	0.50	0.30	69.0 ^a
Φ_T	0.76	0.52	0.72	<< 0.01 ^a
τ_F (ns)	2.4 ^b , 0.45 ^c	0.014	1.4 ^d	--

τ_F - Fluorescence life time [22-23], ISC- Intersystem crossing ($S_1 \rightarrow T_1$) [27-28]

Φ_T - Triplet quantum yield [24-26], 1E and 3E - Singlet and triplet excited energies of dyes [24].

a- $\text{C}_2\text{H}_5\text{OH}$, b- CH_3CN , c- CH_3OH and d- H_2O . 3-MethoxyFlavone (3MF)

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