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Ultrafast Excited State Dynamics of S2 and S1 States of Tri-phenyl Methane Dyes

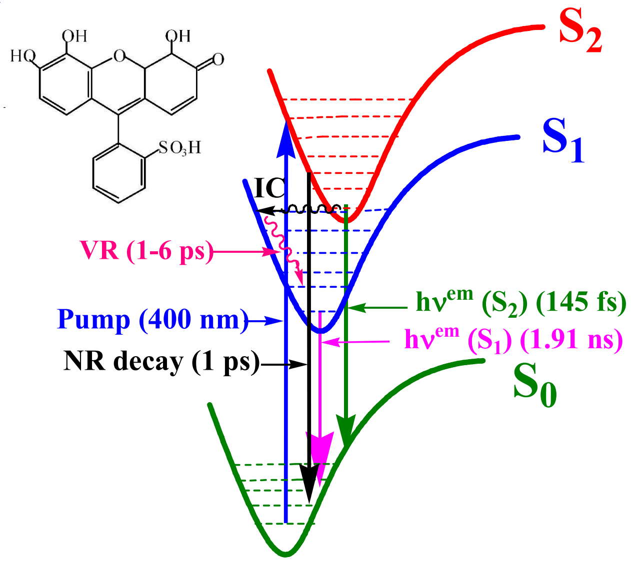
Pallavi Singhal[†] and Hirendra N. Ghosh[#, *]

[†]Health Physics Division, [#]Radiation & Photochemistry Division,
Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, INDIA,

* To whom correspondence should be addressed. E-mail: hnghosh@barc.gov.in Fax: (+) 91-22-25505331/25505151

Abstract:

Excited state dynamics of S2 and S1 states for series of TPM dyes, pyrogallol red (PGR), bromo pyrogallol Red (Br-PGR), aurin tri carboxylic acid (ATC) have been monitored by using ultrafast transient absorption and fluorescence up-conversion techniques. Optical absorption studies indicate that all the TPM dyes exist in keto-enol tautomerism depending upon the pH of the solution. Interestingly all the TPM dyes give S2 emission (major emitting state) in addition to weak S1 emission. S2 emission life time as fast as ~150-300 fs and S1 emission lifetime of 2-5 ns was observed depending upon the molecular structure of the dyes. Femtosecond transient absorption studies suggest the presence of ultrafast non-radiative decay channel from S2 state in addition to S2 luminescence. Vibrational relaxation time from hot S1 state is found to be 2-6 ps. Heavy atom effect has been observed in ultrafast relaxation dynamics of Br-PGR.



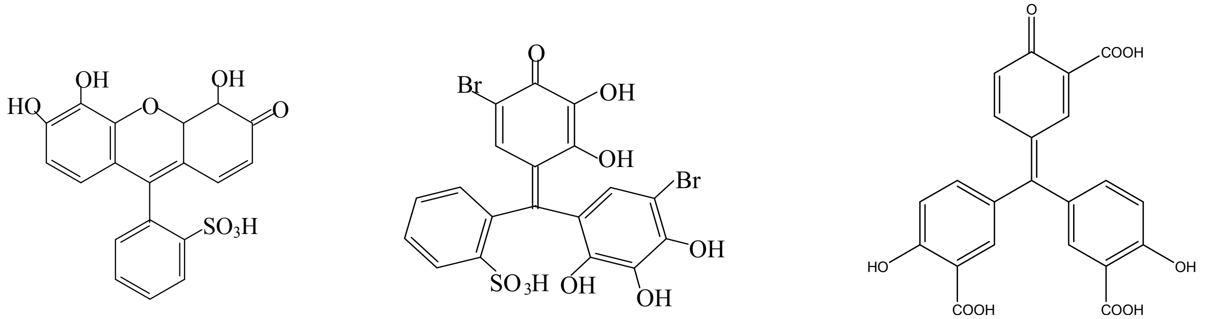
Key words: “S_2 emission”, “Tri-phenyl methane dyes”, “Vibration relaxation”, “Heavy atom effect”, “Non-radiative decay”.

Introduction

Triphenyl methane (TPM) dyes have gained a lot of attention in research activity for more than two decades. Investigations in this area are strongly motivated by both its fundamental importance[1-16] and the large number of practical applications, such as in solar energy conversion[17-21], in textile industry as sensitizers for photoconductivity and in medicine as antibacterial and sterilization agents during blood transfusions[22-24]. The photoprocesses in TPM dyes are intrinsically interesting but complicated and various time-resolved techniques have been used to understand the molecular structure, electronic states, and relaxation dynamics[25-30]. However, still there are many fundamental questions that have to be answered concerning the mechanism and dynamics of radiative and non-radiative transitions and vibronic relaxations including those from the higher excited electronic states. It is well documented in the literature that fluorescence usually occurs from lowest excited singlet state (S_1) which ever electronic states are excited for that molecule. According to Kasha, emission take place from S1 state due to rapid radiationless decay from higher excited states. However exception to this rule exist in molecules like azulene[31] and in some TPM dyes[8, 15.16] (like malachite green MG) that give S2 fluorescence after exciting them at higher excited states. In literature excited state decay dynamics of the S2 states for some of the TPM dyes has been discussed by using fluorescence upconversion technique[8, 15.16].

The major applications of triphenylmethane (TPM) dyes arise due to their intense absorption in visible region which is very necessary to enhance the efficiency of a solar system. These molecules are used as sensitizers in dye-sensitized solar cell due to broad absorption in the visible region and good affinity towards TiO_2nanoparticles[18-20]. However, the photo current efficiency of the solar cells made by using these TPM dyes (e.g., bromopyrogallol red and pyrocatecol violet) were found to be <1%[19.] The mechanism and hence the reason for the low efficiency of these solar cells are not well understood. In our earlier investigation we have demonstrated ultrafast interfacial electron transfer dynamics of these dyes sensitized on TiO_2 nanoparticles by exciting the samples at 620 nm where excitation of upper excited states are not involved. Recently we have reported that these TPM dyes can be used as molecular adsorbate in super-sensitized quantum dot solar cell system[32, 33] for their affinity towards different quantum dot (CdSe and CdS etc) materials and suitable excited and ground state energy levels for charge transfer process with QD materials. In super-sensitized quantum dot materials LUMO and HOMO level of molecular adsorbate lies above the conduction band and valence band of the QD materials and both molecular adsorbate and QD materials can sensitize TiO_2 nanoparticles. In our earlier studies we have demonstrated that composite of CdSe/pyrogallol red (PGR) and CdSe/aurin tricarboxylic acid (ATC) can act as a supersensitizer system where both ATC and PGR can inject electron from both of their S1 and S2 state onto QD and at the same time they can act as a hole transporting agent from QD which result in grand charge separated states[32, 33]. Dynamics of photoexcited states of these TPM dyes by exciting the molecules to upper excited states is not discussed by us and is not reported in the literature. It is very important to understand the excited state dynamics which includes both radiative and non-radiative process of the TPM dyes which are frequently used in dye-sensitized solar cell to maximize the efficiency and also as a supersensitizer in solar cells.

In the present investigation we have chosen three TPM dyes, pyrogallol red (PGR), bromopyrogallol red (Br-PGR), aurin tri carboxylic acid (ATC) (Chart 1) to study the excited state dynamics by exciting the molecules at upper excited states. Photoluminescence studies on these TPM dye molecules suggest the presence of multiple emitting states (S2 and S1) while exciting at higher excited states. Photo-excitation of upper excited states leads to radiative processes like S2 and S1 emission and non-radiative processes like internal conversion (IC), vibrational relaxation (VR) and intersystem crossing (ISC) which takes place in fast and ultrafast time scale. To understand the total dynamics of photo-excited TPM dyes molecules in early time scale it is very important to monitor the excited states using transient time-resolved absorption technique in addition to fluorescence up-conversion technique which give information only about radiative processes. In the present investigation we have carried out femtosecond transient absorption and fluorescence up-conversion experiments to study the excited state dynamics of the TPM dyes in ultrafast time-scale after exciting at 400 nm laser pulse. Control pH experiments in buffered condition for all these dyes have been discussed in the present investigation to see the effect of pH on excited state dynamics of different isomers (keto-enol). Concentration dependent steady state and transient measurements have been carried out for all the TPM dyes to verify aggregate formation of the above dye molecules at higher concentration.



Pyrogallol Red (PGR) **Bromo Pyrogallol Red (Br-PGR)** **Aurin tri carboxylic Acid (ATC)**

Chart 1: Molecular Structure of the triphenyl methane dyes studied in the present studies

2. Experimental Section:

a) Chemicals:

Pyrogallol red (PGR), bromo-pyrogallol red (Br-PGR), aurin tri-carboxylic acid (ATC) and toluene were purchased from Aldrich and was used without further purification. Nanopure water was used for making aqueous solutions.

b) Steady State Absorption and Emission Spectrometer:

Steady-state absorption spectra were recorded on a Thermo-Electron model Biomate spectrophotometer. Fluorescence spectra, which were corrected for the wavelength dependence of the instrument sensitivity, were recorded using Hitachi model 4010 spectrofluorimeter.

c) Time-Correlated Single Photon Counting (TCSPC):

Time resolved fluorescence measurements were carried out using a diode laser based spectro fluorometer from IBH (UK). The instrument works on the principle of time-correlated single photon counting (TCSPC). In the present work, a 406-nm laser light (FWHM <100ps) was used as the excitation light sources and a TBX4 detection module (IBH) coupled with a special Hamamatsu PMT was used for fluorescence detection.

d) Femtosecond Fluorescence Up-conversion Setup:

In femtosecond fluorescence up-conversion setup (FOG 100, CDP), FLU was excited at ~400 nm and emission was monitored at 510 nm (emission maxima). The second harmonic (SH) of a mode locked Ti:sapphire laser (CDP Corp., Moscow, Russia, 82.2 MHz repetition rate) pumped by a 5 W DPSS laser was used for excitation[34]. The SH was generated in a type I BBO angle-tuned phase-matched nonlinear crystal with 1 mm thickness. Optical delay between the excitation and the gate pulse was varied using a delay rail (6.6 fs per steps) at the path of the gate pulses. The up-converted signal was measured with a photon counter after passing through a proper band-pass filter and a double monochromator. In all of these measurements, the samples were taken in a rotating cell (0.4 mm path length) to have a better heat dissipation and thus to avoid the photodegradation of the dye. For the measurements of fluorescence transients, polarization of the SH beam was set to the magic angle (54.7°) with respect to the observed horizontally polarized fluorescence signal using Berek wave plate arrangement (CDP Corp., Moscow, Russia). The fluorescence signal from the sample was up-converted in another nonlinear BBO crystal (thickness 0.5 mm) using the Ti:sapphire fundamental beam as the gate pulse. A cross correlation of fundamental and the SH displayed a full width at half-maxima (fwhm) of ~250 fs for the instrument response function (IRF). Femtosecond transients were fitted by convolution analysis using a Gaussian shape for the IRF.

e) Femtosecond Transient Absorption Studies: The femtosecond tunable visible spectrometer has been developed based on a multi-pass amplified femtosecond Ti:sapphire laser system supplied by Thales, France. The pulses of 20 fs duration and 4 nJ energy per pulse at 800 nm obtained from a self-mode-locked Ti-Sapphire laser oscillator (Synergy 20, Femtolaser, Austria) were amplified in a regenerative and two-pass amplifier pumped by a 20W DPSS laser (Jade) to generate 40 fs laser pulses of about 1.2 mJ energy at a repetition rate of 1 kHz. The 800 nm output pulse from the multi-pass amplifier is split into two parts to generate pump and probe pulses. In the present investigation we have used frequency doubled 400 nm as excitation sources. To generate pump pulses at 400 nm one part of 800 nm with 200 μJ/pulse is frequency doubled in BBO crystals. To generate visible probe pulses, about 3 μJ of the 800 nm beam is focused onto a 1.5 mm thick sapphire window. The intensity of the 800 nm beam is adjusted by iris size and ND filters to obtain a stable white light continuum in the 400 nm to over 1000 nm region. The probe pulses are split into the signal and reference beams and are detected by two matched photodiodes with variable gain. We have kept the spot sizes of the pump beam and probe beam at the crossing point around 500 and 300 micron respectively. The noise level of the white light is about ~0.5 % with occasional spikes due to oscillator fluctuation. We have noticed that most laser noise is low-frequency noise and can be eliminated by comparing the adjacent probe laser pulses (pump blocked *vs* unblocked using a mechanical chopper). The typical noise in the measured absorbance change is about <0.3%. The instrument response function (IRF) for 400 nm excitation was obtained by fitting the rise time of the bleach of sodium salt of *meso* tetrakis (4 sulfonatophenyl) porphyrin (TPPS) at 710 nm and found to be 120 fs [35]. The energy used in the transient measurements is ~ 1μJ with pump beam diameter of 400 μm. Now for 400 nm laser excitation laser fluency and number of photons absorbed by dye molecules is calculated to be $8x10^{-4}$ J/cm^2 and $1.6x10^{15}$ photons/cm^2 respectively. In this experimental condition the number of photons absorbed by dye molecule will be much less than one which excludes the possibility of multiple excitations. All the samples were dissolved in nanopure water. The dye solution was circulated to avoid sample bleaching during the course of the experiment. The data analysis and fitting at individual wavelengths were carried out by Lab-View program.

3. Results and Discussion:

a) Optical absorption Studies:

It is widely reported in literature that TPM dyes display many interesting spectral features which is a direct consequence of their structure and their interaction with the surrounding environment[1, 5]. These dyes are also very sensitive to change in pH of the solution[1] and it is reported in literature that TPM dyes exist in different isomers (keto-enol) at different pH. To understand the excited state dynamics of different isomers of tri-phenyl methane (TPM) dyes in ultrafast time scale it is very important to carry out steady state absorption and emission studies by controlling the pH of the system. In the present investigation we have carried out optical absorption studies of all the TPM dyes in water and in 0.1 M phosphate buffer (pH 7). Interestingly the aqueous solution of all TPM dyes is acidic. In aqueous solution the sulphonic acid group easily dissociates with releasing a proton, as a result the pH of the solution goes below normal and become acidic. We have measured the pH of all the aqueous solution of TPM dyes and found that the pH of PGR in water is 4 while for Br PGR is 4.2 and for ATC is 4. We have measured and reported second pKa values of PGR and Br PGR and found to be 6 and 4.4

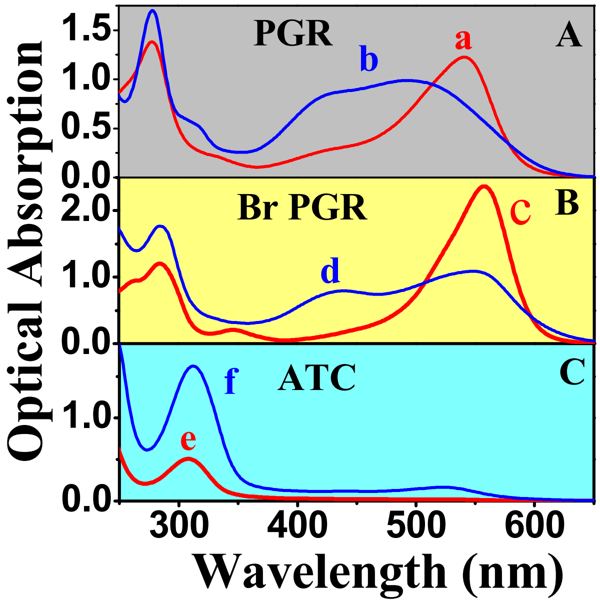


Figure 1: Steady state absorption spectra of A: (a) PGR 50 uM 7 pH buffer (red) (b) PGR water (Blue) B: (c) Br PGR 50 µM 7 pH buffer (red) (d) Br PGR water (Blue) C: (e) ATC 50 uM 7 pH buffer (red) (f) ATC water (Blue).

respectively (SI Figure 1, 2, 3 and SI Table 1) which matches exactly with the literature values[36]. Our experiental observation and literature reports suggest that TPM dyes will exist as H_3A^- in aqueous solution and as H_2A^{-2} in pH 7 buffer. So we can conclude that TPM dyes will exist as enol form (H_3A^-) in water and keto form (H_2A^{2-}) in pH 7 buffer. Figure 1 shows the optical absorption spectra of all three TPM dyes PGR (upper panel A), Br-PGR (middle panel B) and ATC (lower panel C) in pH 7 buffer and in water. An absorption band in UV region and another broad band in visible region have been observed clearly for all three TPM dyes. It is interesting to see that PGR in water shows an absorption band in UV region peaking at 278 nm with broad absorption band in the visible region (350-600 nm range) with absorption peak at 492 nm and a hump at 420 nm. In buffer solution no change was observed in UV band, however visible band shows absorption peak at 540 nm with a small hump at 413 nm. On the other hand Br-PGR in water shows an absorption band in UV region peaking at 284 nm with broad absorption band in the visible region (350-620 nm range) with two absorption peaks at 428 nm and 548 nm. However in buffer a single peak was observed at 557 nm in the visible region with UV peak in the same region peaking at 284 nm. Interestingly for ATC both in water and in buffer solution UV was observed peaking ~310 nm and a very low intensity visible band in 350-600 nm region peaking at 520 nm. Interestingly in buffer condition intensity of both the bands gets drastically reduced for ATC. It is reported in the literature[1, 8, 15, 16] that many tri-phenyl methane dyes have two absorption bands: one in the UV region which has been attributed to $S_0 \rightarrow S_2$ transition and another in the visible region which has been attributed to $S_0 \rightarrow S_1$ transition[8]. In the present investigation in all three TPM dyes we have observed a UV band which can be attributed to $S_0 \rightarrow S_2$ transition and the visible absorption band that can be attributed to $S_0 \rightarrow S_1$ transition. It is interesting to see that optical absorption spectra of PGR and Br-PGR in both keto and enol form are different. However in case of ATC no such change was observed except extinction coefficient of keto form reduces drastically as compared to enol form and in the visible region it shows a featureless absorption band without any absorption peak. Structural changes in keto-enol tautomerism for all the TPM dyes are discussed in detail in supporting information (SI Scheme 1). It is clear from the structure that both PGR and Br-PGR are non-symmetrical in structure however ATC has symmetrical structure. Due to non-symmetrical structure of PGR and Br PGR, polarization in X and Y direction is different, as a result we have observed two peaks in visible region spectra of PGR and Br PGR. On the other hand polarization will be same in both the direction for ATC due to its symmetrical structure due to which we have observed a single peak in the visible region. It is reported in literature[37] that tri-phenyl methane dyes tend to form aggregates at higher concentration in water. Mandel and co-workers[37] reported formation of aggregates for crystal violet (CV, a tri-phenyl methane dye) in the concentration range of > 1mM in aqueous solution. We have also carried out concentration dependent measurements of all three dyes (1-100 μM range) both in water and at pH7 buffer to see the formation of aggregates and results are shown in supporting information (SI Figure 4). No sign of aggregate formation was observed for all the three TPM dyes from optical absorption studies. Concentration dependence (1-100 μM range) optical absorption at a particular wavelength shows linear increment with concentration which also indicates formation non-aggregates in the concentration range of our measurements.

b) Emission Studies:

To understand the photophysics of TPM dyes it is very important to carry out the emission and excitation spectroscopy. We have carried out emission and excitation measurements in pH 7 buffer solution to maintain constant pH of the solution. No emission was observed from both PGR and Br-PGR by exciting at different wavelengths in both S2 and S1 region. This might be due to presence of pyrogallol (three consecutive OH group in the same benzene ring as seen in Chart 1) and catecholate moiety in PGR and Br-PGR which is exposed to water molecules and forms hydrogen bond. On formation of H-bond with water molecules the non-radiative decay channel becomes very efficient as a result we don't see much emission from both PGR and Br-PGR. However on exciting ATC in pH 7 buffer at 360 nm a broad emission band was observed peaking at 485 nm. As the $S_0 \rightarrow S_1$ transition takes place from 400 - 600 nm region so the emission band cannot be attributed to pure S1 emission. The broad emission spectrum can be attributed to combination of both S2 and S1 emission.

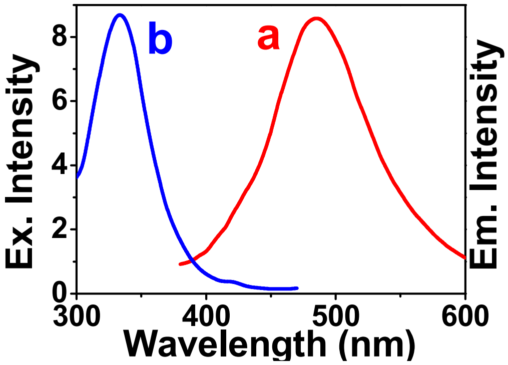


Figure 2: Steady state a) emission spectra (λ_{ex}=360 nm) and (b) excitation spectra (λ_{em}=485 nm) of ATC in pH 7 buffer.

It is interesting to see that excitation spectra (Figure 2b) matches closely with the $S_0 \rightarrow S_2$ transition band in optical absorption spectra of ATC in pH 7 buffer (Figure 1). It was also reported earlier that many derivatives of TPM dyes give S2 emission[8, 15, 16]. So from our emission and excitation spectroscopic studies we come to a conclusion that S1 state of ATC dye is less emittive but on excitation of S2 band we can observe clear S2 emission. We have also carried out emission measurements exciting the sample at 450 and 480 nm which primarily excite the S1 states where no emission was observed. These results are shown in supporting information. We have realized that it is very important to know the relative energy difference between the Franck-Condon states (S0, S1 and S2) of all the TPM dyes to understand excited state dynamics of different excited states. In our earlier investigation[20] we have reported ground state redox potential values of all the TPM dyes. Energy difference between S0 and S1 state and S0 to S2 state for all the three TPM dyes were determined from onset absorption as measured in steady state optical absorption studies. These values have been added to ground state redox level to get the S1 and S2 state redox levels. The energy difference between S0, S1 and S2 states along with their redox levels for all three dyes are shown in Supporting Information (SI Table 2).

c) Time-resolved Emission Studies:

To understand relaxation dynamics of S2 and S1 states of TPM dyes it is very important to monitor emission lifetimes for all the dyes by exciting and monitoring at different wavelengths. Although the emission intensity for all the TPM dyes is very low still we have carried out emission lifetime measurements. Figure 3 shows emission decay traces of TPM dyes in pH 7 buffer after exciting the samples at 406 nm and monitoring the emission at 550 nm. The emission decay traces for all the TPM dyes can be fitted multi-exponentially where major component can be fitted with pulse-width limited time (Table 1). In steady state emission studies we have observed that emission arises from both S2 and S1 state where S2 emission dominates over S1. It is reported in the literature[15, 16] that S2 emission lifetime is faster as compared to that of S1 emission. The pulse-width limited decay in Figure 3 can be attributed to S2 emission and longer components can be attributed to S1 emission life time. It is interesting to see that contribution of pulse-width limited decay is more in PGR and Br-PGR as compared to that of ATC. This might be due to presence of pyrogallol moiety (three consecutive OH group) and catecholate moiety in PGR and Br-PGR due to which non-radiative decay facilitate through H-bonding and therefore S2 state emission life time of PGR and Br-PGR is shorter as compared to that of ATC. We have also carried out time-resolved emission measurements after exciting the sample at 445 nm which excite purely S1 state of the TPM dyes, similar trends of emission decay was observed which is dominated by non-radiative decay process in all the TPM dyes. The results are incorporated in the Supporting Information (SI Figure 7 and SI Table 3). We have also carried out concentration dependent emission lifetime measurements for all three dyes and

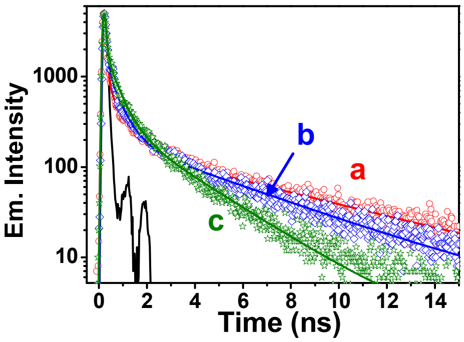


Figure 3: Time resolved emission studies of (a) PGR (b) Br PGR (c) ATC in pH 7 buffer after exciting the samples at 406 nm and monitoring the emission at 550 nm. Concentrations of TPM dyes were kept 5 μM .

Table 1: Kinetic parameters for the time-resolved emission decay kinetics for the TPM dyes at different concentrations after exciting the samples at 406 nm and monitoring at 550 nm in pH 7 buffer. Concentrations of TPM dyes were kept 5 μM.

	τ_1	τ_2	τ_3
PGR	<100 ps (90 %)	0.78 ns (9%)	6.5 ns (1%)
Br PGR	<100 ps (89%)	0.531 ns (10%)	4.56 ns (1%)
ATC	<100 ps (85%)	0.5 ns (13%)	2.56 ns (2%)

observed that emission lifetime changes marginally for both PGR and Br-PGR however in case of ATC emission decay becomes marginally faster with increase in concentration (SI Table 4). This might be due to formation of very weak aggregates of ATC in water due to its near planner structure. Although weak aggregate formation was never indicated in steady state absorption studies. We have also carried out pH dependent measurements for all three dyes and results are shown in supporting information (SI Figure 9 and SI Table 5). Concentration and pH (buffer pH 3 and pH 7) dependent emission life time measurements are reported in supporting information (SI Figure 8 and SI Table 4), where no pH dependent lifetime was observed for the TPM dyes. As we have observed in both steady state and time-resolved luminescence measurements that emission from all the TPM dyes dominated by S2 emission and decays with pulse-width limited time. So to monitor S2 emission life time from all the TPM dyes it is important monitor the emission using Femto-second fluorescence up-conversion studies.

d) Femtosecond fluorescence up-conversion studies:

In our sub-nanosecond time-resolved emission studies we have observed that S2 emission life time is too fast compared to time resolution of the instrument. As a result it is difficult to comment on S2 emission lifetime using nanosecond time resolution measurements. It is reported in the literature[15,16] that S2 state lifetime of malachite green which is also a tri-phenyl methane dye is in the range of ~100 fs. Earlier Yoshizawaet al.[15] and Bhasikuttan et. al[16] have investigated the relaxation dynamics of the S2 excited state of malachite green by using fluorescence upconversion spectroscopy and reported S2 emission lifetime to be ~ 130 fs. So to monitor S2 state for all the TPM dyes in the present studies it is very important to measure the excited state

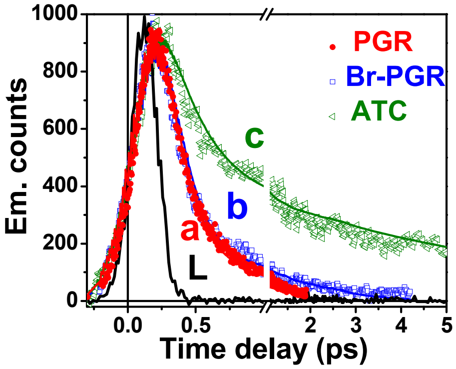


Figure 4. Fluorescence up-conversion emission decay trace of (a) PGR, (b) Br-PGR, (c) ATC in pH 7 buffer at 520 nm after exciting at 400 nm laser pulse (FWHM = 200 fs). Concentrations of TPM dyes were kept 50 μM.

lifetime in ultrafast time scale. To find out S2 state emission lifetime we have carried out time-resolved up-conversion measurements for all the TPM dyes in pH 7 buffer by exciting the samples with 400 nm laser light and monitoring the emission at 520 nm and results are shown in

Table 2: Kinetic parameters for the fluorescence up-conversion emission decay traces for the TPM dyes in pH 7 buffer at 520 nm after exciting at samples at 400 nm laser light.

Sample	τ_1	τ_2
PGR	145 fs(89.5%)	>1 ps(10.5%)
Br PGR	150 fs(91.7%)	>2 ps(8.3%)
ATC	290 fs (75.7%)	>10 ps (24.3%)

Figure 4. To avoid artifacts due to Raman lines we have deliberately keep the monitoring wavelength in the red region. Interestingly we have observed the same trend as in nanosecond time scale resolution PGR and Br PGR has almost similar decay pattern and ATC has higher emission lifetime. The higher emission lifetime of ATC compared to both PGR and Br PGR might be due to pyrogallol moiety which is present in both PGR and Br PGR due to which the relaxation rate is fast in both PGR and Br PGR as compared to ATC. All three dyes decay biexponentially with faster component corresponds to S2 state lifetime and longer component corresponds to S1 state lifetime. For PGR and Br PGR S2 state lifetime is found to be of the order of ~150 fs. Interestingly S2 state emission lifetime for ATC was found to be 290 fs.

e) Ultrafast Transient absorption spectroscopy of TPM dyes:

Although nanosecond time-resolved emission and femtosecond fluorescence up-conversion measurements gives us an idea of decay dynamics of both S1 and S2 states of all the TPM dyes, however from luminescence measurements it is difficult to make comment on the population and relaxation dynamics of different excited states. In addition to that, luminescence spectroscopy gives us the idea of only radiative transition, and unable to monitor the non-radiative transition of the photoexcited states of the dyes. Now to monitor total dynamics we have carried out femtosecond transient absorption spectroscopy for both PGR and Br-PGR in water by exciting the samples at 400 nm. In our earlier investigation[20] we have demonstrated ultrafast interfacial electron transfer dynamics for both PGR and Br-PGR sensitized TiO_2 nanoparticles exciting the samples at 620 nm where free dyes absorption was negligible. As a result we could not monitor the excited state dynamics of free PGR and Br-PGR. Figure 5 shows the transient absorption spectra of photoexcited PGR (upper panel) and Br-PGR (lower panel) in water at different time delay, which comprises a negative absorption band in 500-700 nm region for PGR and in 500-750 nm region for Br-PGR at early time scale and at later time scale positive absorption band from 620-900 nm for both PGR and Br-PGR. The negative absorption (bleach) appears due to photoexcitation of the ground state molecules, where the molecules have optical absorption in the same spectral region. The positive transient absorption signal of PGR and Br-PGR can be attributed to the excited singlet (S1) state absorption. It is interesting to see that positive absorption in case Br-PGR is much lower as compared to that of PGR. Lower positive transient absorption signal of S1 state in case of Br- PGR might due to presence of heavy atom effect, which can facilitate ultrafast deactivation of S1 state to either ground state or to the excited triplet state. Earlier Jortner and co-workers[38] have reported the effect of internal heavy atom on the relaxation dynamics of anthracene and 9 bromo derivative of anthracene. They have clearly shown that inter system crossing from S1 state to T1 state is faster which leads to faster nonradiative decay rate in case of bromo derivative. Similarly Pant and coworkers[39] demonstrated internal heavy atom effect on the radiative and non-radiative rate constants in xanthene dyes. They have clearly shown emission quantum yield decreases and phosphorescence quantum yield increases from Fluorescein to 2,7-dichlorofluorescein to 2,7-dibromofluorescein. The increment of phosphorescence quantum yield has been assigned due to large spin orbit

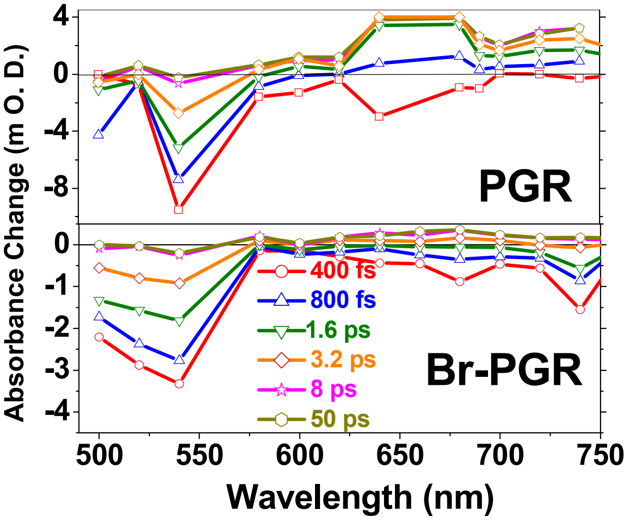


Figure 5. Transient absorption spectra of (A) PGR (upper panel) and (B) Br-PGR in water at different time delay after excitation at 400 nm laser light.

coupling. Similarly in the present investigation due to higher SO (spin - orbit) interaction in Br-PGR intersystem crossing rate is higher as result singlet state absorption is less as compared to that of PGR. To reveal excited state dynamics of both PGR and Br-PGR we have monitored the kinetics at 540 nm and at 700 nm and results are shown in Figure 6. We have also carried out transient absorption studies for both PGR and Br-PGR in pH 7 buffer solution by exciting the samples at 400 nm laser pulse and monitor the dynamics at key wavelengths and results are shown in supporting Information (SI Figure 10 and SI Table 6). All the kinetic traces in Figure 6 are fitted multi-exponentially and shown in Table 3. It is interesting to see that bleach at 540 nm for PGR recovers multi-exponentially with time constants 0.1 ps (50%), 1 ps (46.5%) and > 500 ps (3.5%). However kinetic trace at 700 nm can be fitted in bi-exponential growth components with time constants 1 ps (78%) and 6 ps (22%) and finally the transient decay signal with time constants 90 ps (-18 %) and > 500 ps (-82 %). The bleach appears due to excitation of ground state molecules by 400 nm laser light. So the bleach recovery at 540 nm can be attributed to the de-excitation of excited molecules to the ground state which include both radiative and non-radiative pathways. As we have observed S2 luminescence lifetime ~ 145 fs, so ~0.1 ps component can be attributed to radiative transition and 1 ps recovery component can be attributed to non-radiative transition to the ground state. Interestingly at 700 nm bi-exponential

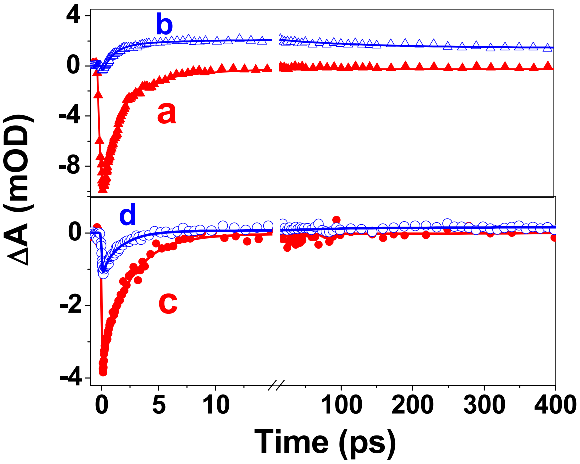


Figure 6. Top Panel: Kinetic traces at (a) 540 nm and b) 700 nm in water for PGR. **Bottom Panel:** Kinetic traces at (c) 540 nm and (d) 700 nm in water for Br-PGR.

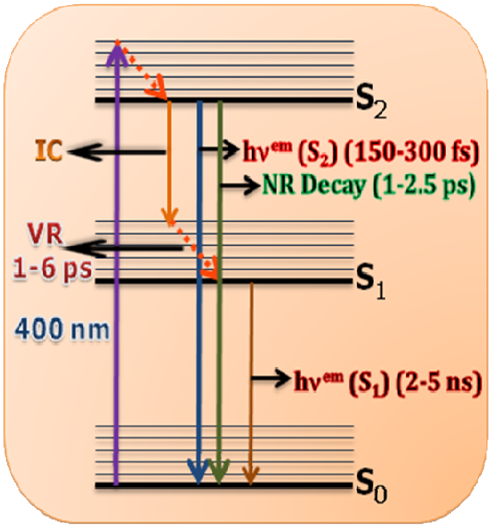
positive growth has been observed. At 400 nm both S_2 state and higher vibration state of S_1 states of PGR can get excited as indicated from optical absorption spectra (Figure 1). So the growth signal can be attributed to either internal conversion from S_2 to S_1 and/or vibrational relaxation from higher vibrational states of S_1 to lower vibrational state of S_1. Finally the longer decay component > 500 ps can be attributed to excited S_1 state lifetime which is reflected from longer S1 state emission lifetime. Interestingly for Br-PGR at both 520 nm and at 700 nm we have observed bleach due to presence of ground state absorption in that spectral region (Figure 1). Here also we have observed fast bi-exponential recovery at 520 nm which can be attributed to both radiative and non-radiative transition. As we have observed S2 emission lifetime of Br-PGR ~ 150 fs, so 0.11 ps recovery component can be attributed to radiative transition and the slower 2.5 ps component can be attributed non-radiative transition. In the present investigation we have observed lower excited state absorption for Br- PGR as compared to PGR. This observation is due to presence of heavy atom (Br) which facilitates faster intersystem crossing and/or non-radiative transition to the ground state. We could not carry out ultrafast transient absorption measurements for ATC molecule due to poor solubility in water and low absorption cross-section at 400nm (exciting wavelength).

Table 3: Kinetic parameters for the femto second time-resolved absorption traces for PGR and Br-PGR at different wavelengths after exciting at 400 nm laser light in water.

System	Monitoring wavelength	τ_1	τ_2	τ_3	τ_4
PGR	540	0.1ps (50 %) (recovery)	1ps (46.5 %) (recovery)	>500ps (3.5%) (recovery)	
PGR	700	1ps (78%) (growth)	6ps (22%) (growth)	90ps (-18%) (decay)	>500ps (-82%) (decay)
Br PGR	520	0.11ps (41.6%) (recovery)	2.5ps (57.5%) (recovery)	>500ps (0.9%) (recovery)	
Br PGR	700	0.2ps (25%) (recovery)	1.8ps (68.7%) (recovery)	5 ps (6.3%) (growth)	

e) Ultrafast Relaxation Dynamics of TPM dyes:

In summing up let us discuss the relaxation dynamics of TPM dyes using different fast and ultrafast techniques. The excited state dynamics and relaxation mechanism in TPM dyes after S2-state excitation can be summarized as shown in Scheme 1. Excitation at 400 nm takes the TPM molecules to S2 state and also to the higher vibrational levels in the S1 states. Now from S2 state de-excitation can take place through many channels. Major de-excitation takes place through S2 emission with time constant of 150-300 fs and also through direct non-radiative decay process with time constant of 1-2.5 ps which has been confirmed by both femtosecond fluorescence up-conversion and time-resolved absorption techniques. In addition to radiative and nonradiative decay from S2 state internal conversion (IC) may also takes place which leads to the generation of hot S1 state. Now hot S1 state can be cool down through vibrational relaxation channel with time constants of 1-6 ps which has been monitored from the growth of S1 excited state in transient absorption technique. Finally S1 state lifetime has been measured in the nano-second region (2-6 ns) as observed from both time-resolved emission and transient absorption



Scheme 1. Schematic representation of the proposed relaxation pathways in TPM dyes after S2 excitation. Different relaxation process like S2 emission, S1 emission, vibration relaxation (VR), internal conversion (IC), non-radiative decay (NR) with time scale of the corresponding processes are shown in the scheme.

studies. Interestingly all the relaxation processes are not much affected by change in concentration and pH of the medium.

4. Conclusion:

We have monitored the excited state dynamics of S2 and S1 states of three TPM dyes, pyrogallol red (PGR), bromopyrogallol Red (Br-PGR), aurin tri carboxylic acid (ATC) using time-resolved emission, femtosecond up-conversion and femtosecond transient absorption techniques. Steady state optical absorption measurements suggests that the energy difference between $S_2 \rightarrow S_0$ transition and $S_1 \rightarrow S_0$ transition is more than ~1.5 eV for all the TPM dyes. Steady state emission measurements suggest the presence of both S2 and S1 luminescence where primarily S2 state emission dominates over S1 state emission. Femtosecond upconversion and time-resolved emission studies suggest that the S2 luminescence time for all the TPM dyes is in the range of 150-300 fs, whereas S1 luminescence lifetime is in the range of 2-6 ns. Concentration dependent optical properties (both steady state absorption and emission) suggest that no aggregate formation occur for PGR and Br-PGR, however very weak aggregate formation was detected in ATC molecule. Femtosecond transient absorption studies suggest that in addition to S2 luminescence, non-radiative decay channel from S2 state is also very active in all the TPM dyes. Transient growth signal of S_1 singlet state was observed with time-scale of 1-6 ps for all the TPM dyes and is attributed to the vibrational relaxation in the hot S1 state. Population of S1 state is much lower in Br-PGR as compared to PGR suggesting the effect of heavy atom, which facilitates both intersystem crossing and non-radiative decay process to ground state.

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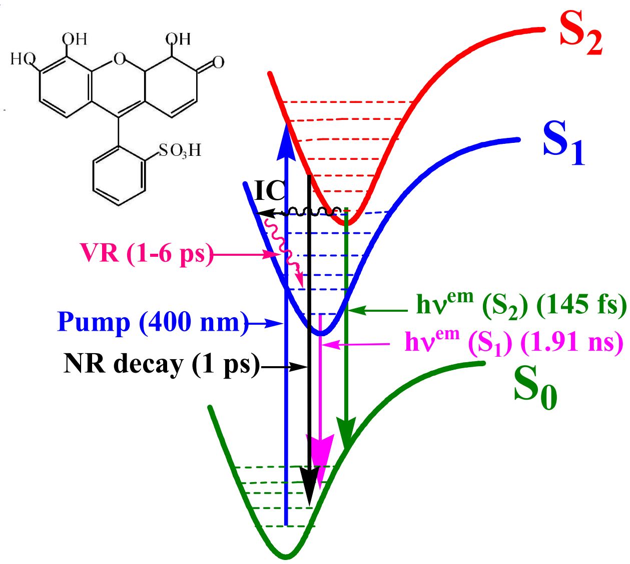
Ultrafast Excited State Dynamics of S_2 and S_1 States of Tri-phenyl Methane Dyes

Pallavi Singhal[†] and Hirendra N. Ghosh[#,] *

[†]Health Physics Division, [#]Radiation & Photochemistry Division,
Bhabha Atomic Research Centre, Trombay, Mumbai – 400 085, INDIA,

* To whom correspondence should be addressed. E-mail: hnghosh@barc.gov.in Fax: (+) 91-22-25505331/25505151



Key words: “S_2 emission”, “Tri-phenyl methane dyes”, “Vibration relaxation”, “Heavy atom effect”, “Non-radiative decay”.