Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

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

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1) Determination of pKa values of the TPM dyes:

Although the pKa values for PGR and Br PGR is available in literature however we have also carried out separate experiments to determine the pKa value for all three TPM dyes namely PGR, Br PGR and ATC.

The equation describing the dissociation of hydrogen at different pH is given by

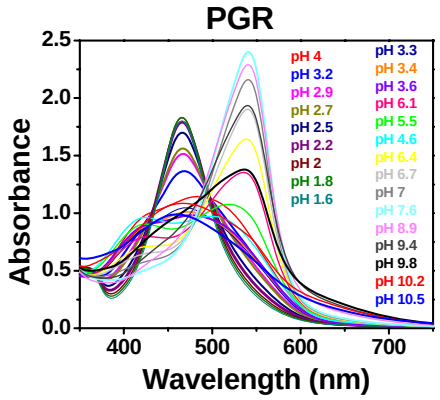
$$H_3A \xleftrightarrow{pKa_1} H_3A^- \xleftrightarrow{pKa_2} H_2A^{-2} \xleftrightarrow{pKa_3} HA^{-3} \xleftrightarrow{pKa_4} A^{-4}$$

In the literature (SI Reference 1) pKa_2, pKa_3 and pKa_4 vales are mentioned for PGR and Br. PGR is listed in SI Table 1. pKa1 vales are not reported in the literature.

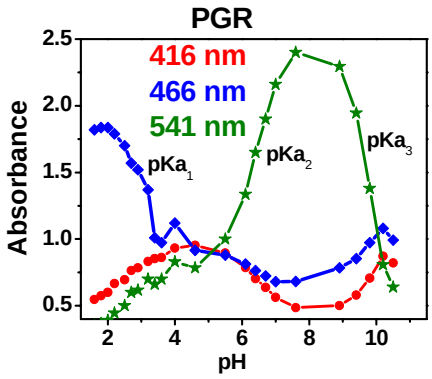
SI Table 1: pKa value for PGR and Br PGR as available in literature (SI Ref 1)

	H_3A^-	pKa_2	H_2A^{-2}	pKa_3	HA^{-3}	pKa_4
PGR	430,505	6	545	9.5	545	12
Br PGR	440,520	4.39	558	9.06	558	11.31

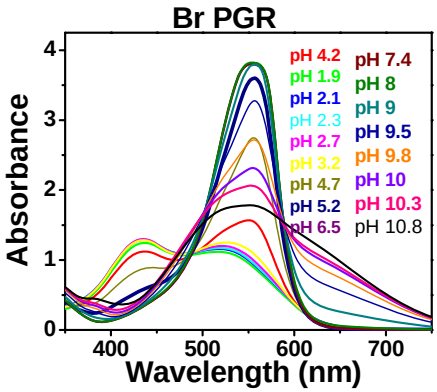
However to reconfirm the above results we have also carried out steady state optical absorption studies of PGR, Br PGR and ATC after changing pH and are shown in figure 1A, 2A and 3A respectively. It is clear from figure that with change in pH the absorption spectra changes for all three dyes. For PGR the peak at 466 nm is shifted to 540 nm with increase in pH from 2 to 10. Similarly for Br PGR the peak at 433 nm is shifted to 550 nm with increase in pH from 2 to 10. However for ATC we did not see any new peak with change in pH but optical density decreases with increase in pH. A plot of pH with absorbance at different wavelengths for all three dyes is shown in Figure 1B, 2B and 3B. It is clear from Figure 1B and Figure 2B that pKa value for PGR and Br PGR matches closely with the reported value. However for ATC the pKa value could not be determined clearly.



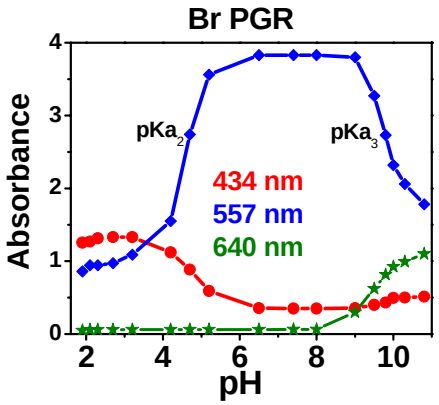
SI Figure 1A: Optical absorption spectra of PGR at different pH.



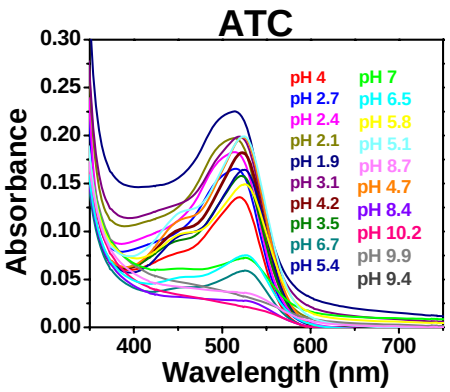
SI Figure 1B: Change of absorption of PGR at different wavelength with pH



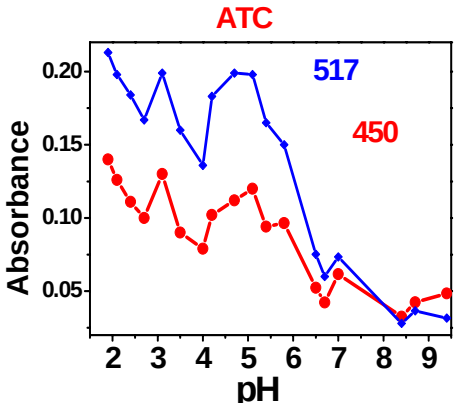
SI Figure 2A: Absorption spectra of Br PGR at different wavelength with pH



SI Figure 2B: Change of absorption of Br PGR at different wavelength with pH



SI Figure 3A: Absorption spectra of ATC at different wavelength with pH



SI Figure 3B: Change of absorption of ATC at different wavelength with pH

It is clear from the above Figure that on changing pH the absorption spectra of PGR and Br PGR changes however ATC absorption spectra is almost same. We have shown different pKa values for both PGR and Br-PGR in Figure 1B and 2B. The second pKa value for PGR and Br PGR is determined to be 6 and 4.4 respectively which matches exactly with the literature values. Although we could not detremine different pKa values for ATC dye through optical absorption spectroscopy by changing the pH of the solution.

SI Reference 1: C. Wygonowski, *Microchem. J.* 1984, 29, 318.

2) Redox levels and energy difference between S0, S1 and S2 Frank Condon states of TPM dyes:

To find out the approximate energy difference between the Franck-Condon states (S0, S1 and S2), we have used cyclic voltametry and optical absorption measurements to determine the relative position and also the energy difference between Frank Condon state of S0, S1 and S2. In our earlier investigation (SI Reference 2) we had measured and reported ground state redox potential for all three TPM dyes. Now we have determined energy difference between S0 and S1 state and S0 to S2 state for all the three TPM dyes 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 SI Table 2.

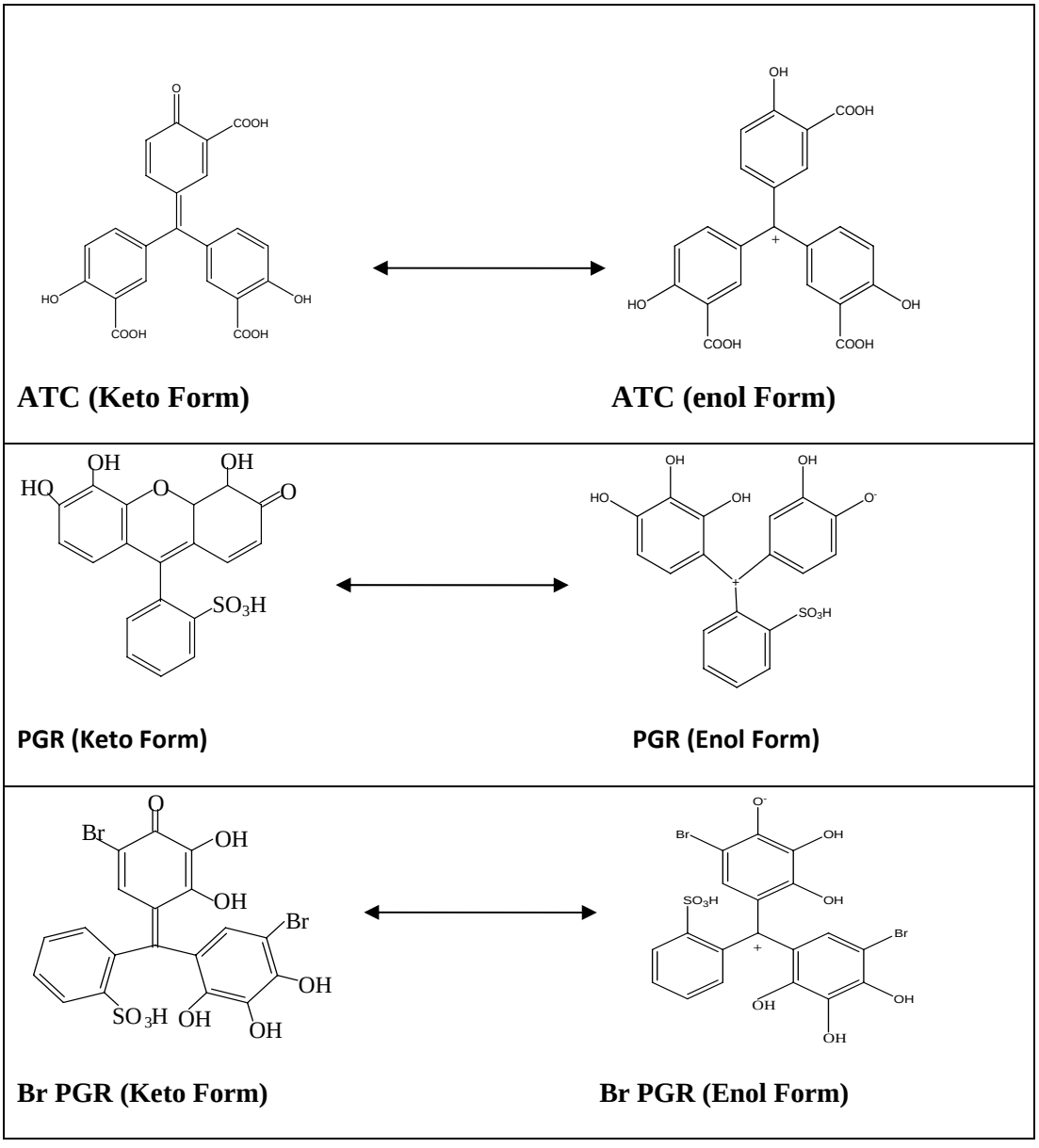
SI Table 2: Redox levels and energy difference between Frank Condon states for PGR, Br PGR and ATC

	E_{Redox} (S0) (eV) vs Ag/AgCl	S0 → S1 (eV)	S0 → S2 (eV)	S1 → S2 (eV)	E_{Redox} (S1) (eV) vs Ag/AgCl	E_{Redox} (S2) (eV) vs Ag/AgCl
PGR	0.478	2 eV	3.98	1.98	-1.522	-3.502
Br PGR	0.458	1.99	3.88	1.89	-1.532	-3.422
ATC	0.475	2.1	3.48	1.38	-1.625	-3.005

SI Reference 2: G. Ramakrishna, H. N. Ghosh, A. K. Singh, D. K. Palit, J. P. Mittal, *J. Phys. Chem. B,* 2001, **105**, 12786-12796.

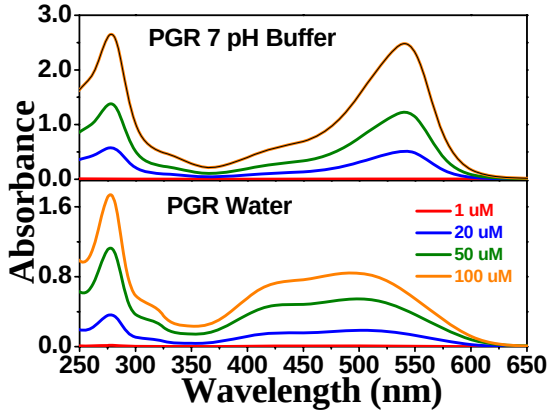
3) Molecule structure of Keto and enol isomers:

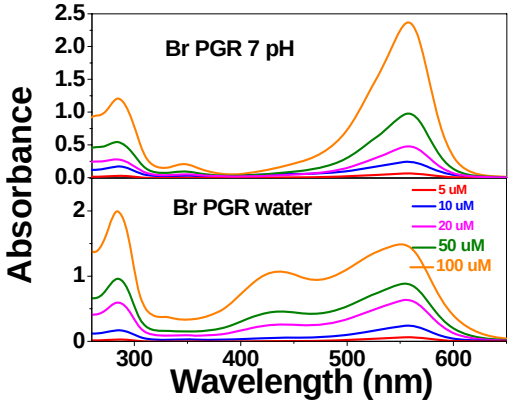
Molecule structure of Keto and enol isomers of different TPM dyes at different pH. At higher pH major form will be keto form while at lower pH molecular structure will be dominated by enol form.

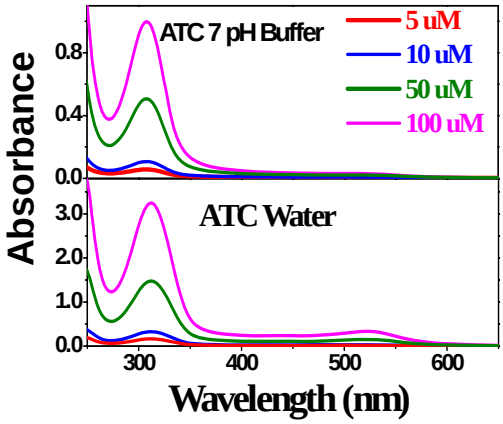


SI Scheme 1: Keto and enol transformation at different pH for all the three TPM dyes.

4) Effect of concentration and pH on optical absorption spectra of TPM dyes:





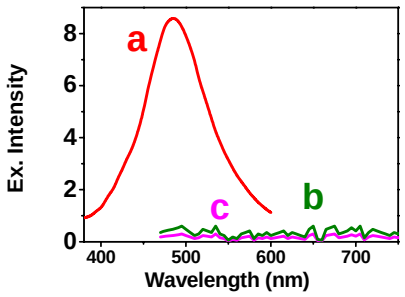


SI Figure 4: Concentration dependent absorption spectrum of PGR, Br PGR, ATC in pH 7 buffer and in water.

SI Figure S4 shows the concentration dependent optical absorption measurements of all three dyes in pH 7 Buffer and in water. The optical absorption studies clearly suggest that there is no aggregate formation both in water and in pH 7 buffer for all the three TPM dyes in the concentration range of 5-100 μM.

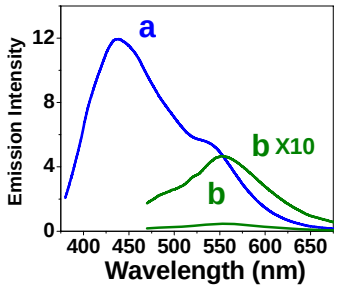
5) Steady state emission studies:

Steady state emission spectra of ATC molecule in pH 7 buffer were recorded after exciting at different wavelengths. We have observed a S2 luminisence by exciting at 360 nm however no emission was observed by exciting S1 band.



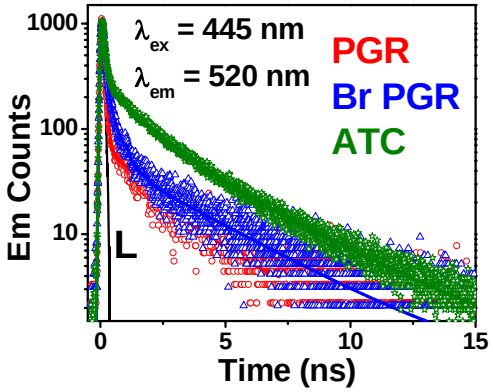
SI Figure 5: Steady state emission spectra of ATC in pH 7 buffer after exciting at a) 360 nm) (b) 450 nm and (c) 480 nm.

Steady state emission studies in toluene shows that on exciting at 360 nm we have observed emission band at 436 nm with a hump at 540 nm which can be attributed to S2 and S1 emission respectively. However on exciting at 450 nm we have observed a very low intensity band at 550 nm which can be attributed to purely S1 emission band.



SI Figure 6: Steady state emission spectra of ATC in toluene after exciting at a) 360 nm and b) 450 nm.

6) Time-resolved emission decay traces of TPM dyes after exciting at 445 nm:

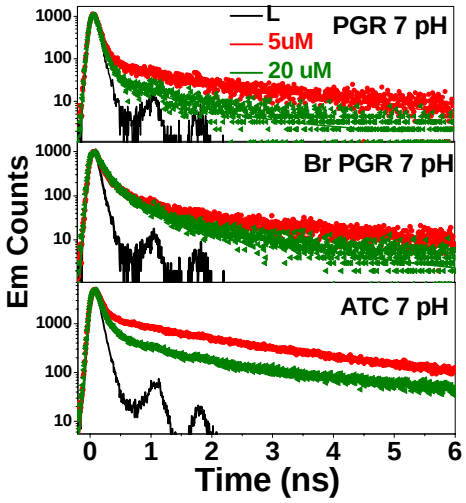


SI Figure 7: Time-resolved emission decay trace of TPM dyes after exciting at 445 nm and monitoring at 520 nm.

SI Table 3: Kinetic parameters for the time-resolved emission decay kinetics for the TPM dyes in pH 7 buffer after exciting at 445 nm and monitoring at 520 nm.

λ_{ex} = 445 nm λ_{em} = 520 nm	τ_1	τ_2	τ_3
PGR	< 100 ps (90%)	1.91 ns (10%)	
Br PGR	< 100 ps (86%)	0.3 ns (5%)	3.35 ns (9%)
ATC	< 100 ps (75%)	1.25 ns (13%)	5 ns (12%)

7) Effect of concentration on time-resolved emission decay traces of TPM dyes:



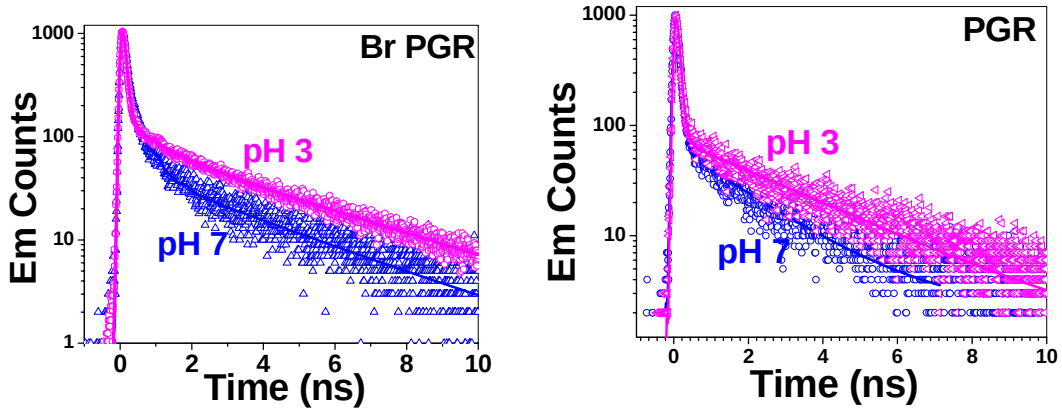
SI Figure 8: Concentration dependent emission decay traces of PGR, Br PGR, ATC in buffer (pH 7) after exciting the samples at 445 nm and monitoring the emission at 520 nm.

SI Table 4: Kinetic parameters for the time-resolved emission decay kinetics for the TPM dyes at different concentrations after exciting the samples at 445 nm and monitoring the emission at 520 nm in pH 7 buffer.

Sample (Concentration)	τ_1	τ_2	τ_3
PGR (5 uM)	< 100 ps (90%)	1.91 ns (10%)	
PGR (20 uM)	< 100 ps (92%)	1.8 ns (8%)	
Br PGR (5 uM)	< 100 ps (86%)	0.3 ns (5%)	3.35 ns (9%)
Br PGR (20 uM)	< 100 ps (88%)	0.26 ns (4%)	3.2 ns (8%)
ATC (5 uM)	< 100 ps (75%)	1.25 ns (13%)	5 ns (12%)
ATC (20 uM)	< 100 ps (80%)	0.66 ns (10%)	4 ns (10%)

8) Effect of pH on time-resolved emission decay traces of TPM dyes:

We have also carried out time-resolved emission measurements for both PGR and Br-PGR molecule in pH 3 and pH 7 -buffered condition. Where in at pH 3 TPM dyes exist in enol form and at pH 7 they exist in keto form. Our time-resolved emission measurements clearly shows that emission lifetime is very similar for both keto and enol form.



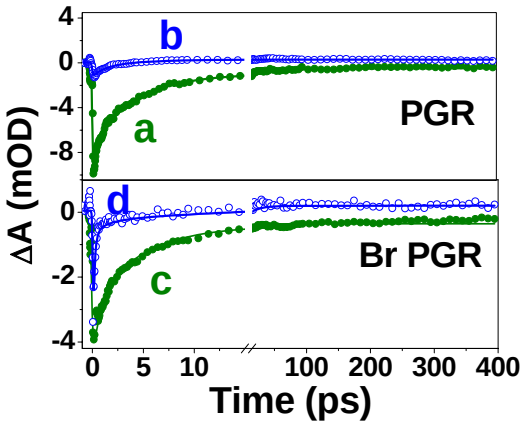
SI Figure 9: pH-dependent emission decay traces of PGR, Br PGR and ATC in both pH 7 buffer and pH 3 buffer after exciting the samples at 445 nm and monitoring the emission at 520 nm.

SI Table 5: Kinetic parameters for the time-resolved emission decay kinetics for the TPM dyes at different pH after exciting the samples at 445 nm and monitoring the emission at 520 nm.

Sample	λ_{em} (nm)	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)
PGR 7 pH 5 uM	520	<0.1 (90%)	1.91 (10%)	
PGR 3 pH 5 uM	520	<0.1 (88%)	2.2 (12%)	
Br PGR 7 pH 5 uM	520	<0.1 (86%)	0.3 (5%)	3.35 (9%)
Br PGR 3 pH 5uM	520	<0.1 (84%)	0.35 (6%)	3.5(10%)

9) Femtosecond transient absorption studies of PGR and Br-PGR in pH 7 buffer.

Transient absorption kinetics at key wavelengths for PGR and Br-PGR in pH 7 buffer.



SI Figure 10. Top Panel: Kinetic traces at (a) 540 nm and (b) 700 nm in pH 7 buffer for PGR. **Bottom Panel:** Kinetic traces at (c) 540 nm and (d) 700 nm in pH 7 buffer for Br-PGR.

SI Table 6: Kinetic parameters for the femto second time-resolved absorption traces for the TPM dyes at different wavelengths after exciting at 400 nm laser light in pH 7 buffer.

System	Monitoring wavelength	τ_1	τ_2	τ_3
PGR	540	0.08ps (20 %) (recovery)	4ps (75%) (recovery)	>500ps (5%) (recovery)
PGR	700	0.3ps (42%) (growth)	2.5ps (53%) (growth)	10 (5%)
Br PGR	520	0.6ps (48%) (recovery)	4.2ps (45%) (recovery)	>500ps (7%) (recovery)
Br PGR	700	0.16ps (82.4%) (recovery)	1.2ps (8.8%) (recovery)	15 (8.8%)