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Photophysics and Photochemistry of Conformationally Restricted Triarylmethanes: Application as Photoredox Catalysts

Sankalan Mondal and Satyen Saha

Abstract

The three aryl rings of triarylmethanes are free to rotate. However this free rotation can be restricted on either by bridging the aryl rings through covalent bonds or through hetero-atoms resulting in the formation of Conformationally Restricted Triarylmethanes (CRT). The photophysics and photochemistry of these CRTs, like 9-arylxanthenes (oxygen bridging), 9-arylthioxanthenes (sulfur bridging), 9, 10-dihydro-9-arylacridines (nitrogen bridging), 9-arylfluorenes (bridging through carbon–carbon covalent bond) have recently been the subject of number studies. Various applications of CRT molecules have been developed out of which application as photoredox catalyst is undoubtedly the most important. In this chapter, we have highlighted recent development of various CRT molecules, their photophysics, photochemistry and an application in the field of photoredox catalysis.

Keywords: conformationally restricted triarylmethanes (CRTs), 9-arylfluorenes, 9-arylxathenes, 9-arylthioxanthenes, photophysics, photochemistry, photoredox catalysis

1. Introduction

Triarylmethanes are compounds in which a carbon atom is linked to three aryl rings (both aromatic as well as heteroaromatic) which may be same or different. The most simple triaryl-methane namely, triphenylmethane was first synthesized by August Kekule in 1872 by heating diphenyl mercury and benzal chloride [1]. Currently, more than thousand references can be found citing this molecule [2]. The development in the synthesis as well as application of
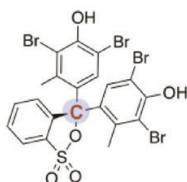
these molecules have attracted various scientists with diverse field of research on this molecular scaffold leading to further high-end applications of these molecules. For example, simple triarylmethane derivatives have shown significant bio-activity against intestinal helminthes, filariae, trichomonads and trypanosomes [3]. Moreover, hydroxy substituted triarylmethanes are known for their antioxidant properties, antitumor activities as well as inhibitors of histidine protein kinases [4, 5]. Letrozole, Vorozole are effective Non-Steroidal Aromatase Inhibitors used commercially for the treatment of breast cancers [6–10]. (**Tram-3**), (**Tram-4**) are common organic dyes based on triarylmethane used in industry (vide **Chart 1**). Further, (**Tram-1**), (**Tram-2**), are common acid–base indicators [11], (**CRT-2**) and (**CRT-10**) are triaryl-methane derivatives widely used as photoredox catalysts to synthesize various useful molecules (vide **Chart 2**) [12–14]. Various thermosetting condensed polynuclear aromatic resins, polymers, materials, drugs are also prepared based on this molecular scaffold (**Figure 1**) [15].

Through various non-covalent interactions, extended networks of hydrogen bonds, steric interactions, cycles/polycycles present in a molecule, the rotation of groups attached to the central carbon are restricted thereby decreasing the conformational mobility enjoyed by the molecules. This change in the conformation of the molecule in general not only modulates different physical properties of the molecule but also influences different photophysical and photochemical properties of the molecule [16, 17]. For example in open chain molecules due to rapid rotation of various bonds the vibrational relaxation of these molecules from the excited state to the ground state through non-radiative pathways are very rapid and these

Phenol Dyes
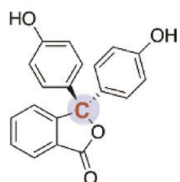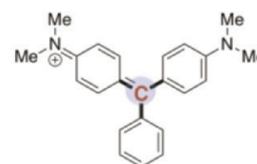
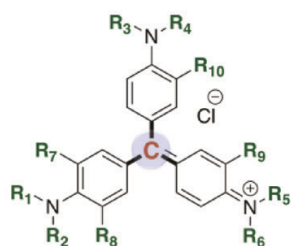Phenolphthalein (**Tram-1**)   Bromocresol green (**Tram-2**)

Malachite green dyes

Malachite green (**Tram-3**)   Brilliant green (**Tram-4**)

Methyl Violet

Methyl violet 2B (R_1 - R_4 = CH_3, R_5 - R_{10} = H) (**Tram-5**).

Methyl violet 6B (R_1 - R_5 = CH_3, R_5 - R_{10} = H) (**Tram-6**)

Methyl violet 10B (R_1 - R_6 = CH_3, R_7 - R_{10} = H) (**Tram-7**)

Methylviolet (R_1 = R_3 = R_3 = R_1 - R_4 = CH_3, R_5 - R_{10} = H) (**Tram-8**)

Fuchsine dyes

Pararosaniline (R_3 = R_4 = CH_3, R_1 = R_2 = R_5 - R_{10} = H) (**Tram-9**)

Fuchsine acid (R_1 - R_6 = H, R_7 = CH_3, R_8 = R_{10} = SO_3Na), R_9 = SO_3^- (**Tram-10**)

New fuchsine (as chloride) (R_1 = R_3 = R_3 = R_5 = R_7 - R_{10} = CH_3, R_2 = R_4 = R_6 = H) (**Tram-11**)

Chart 1. Some common conformationally *flexible* triarylmethanes molecules.
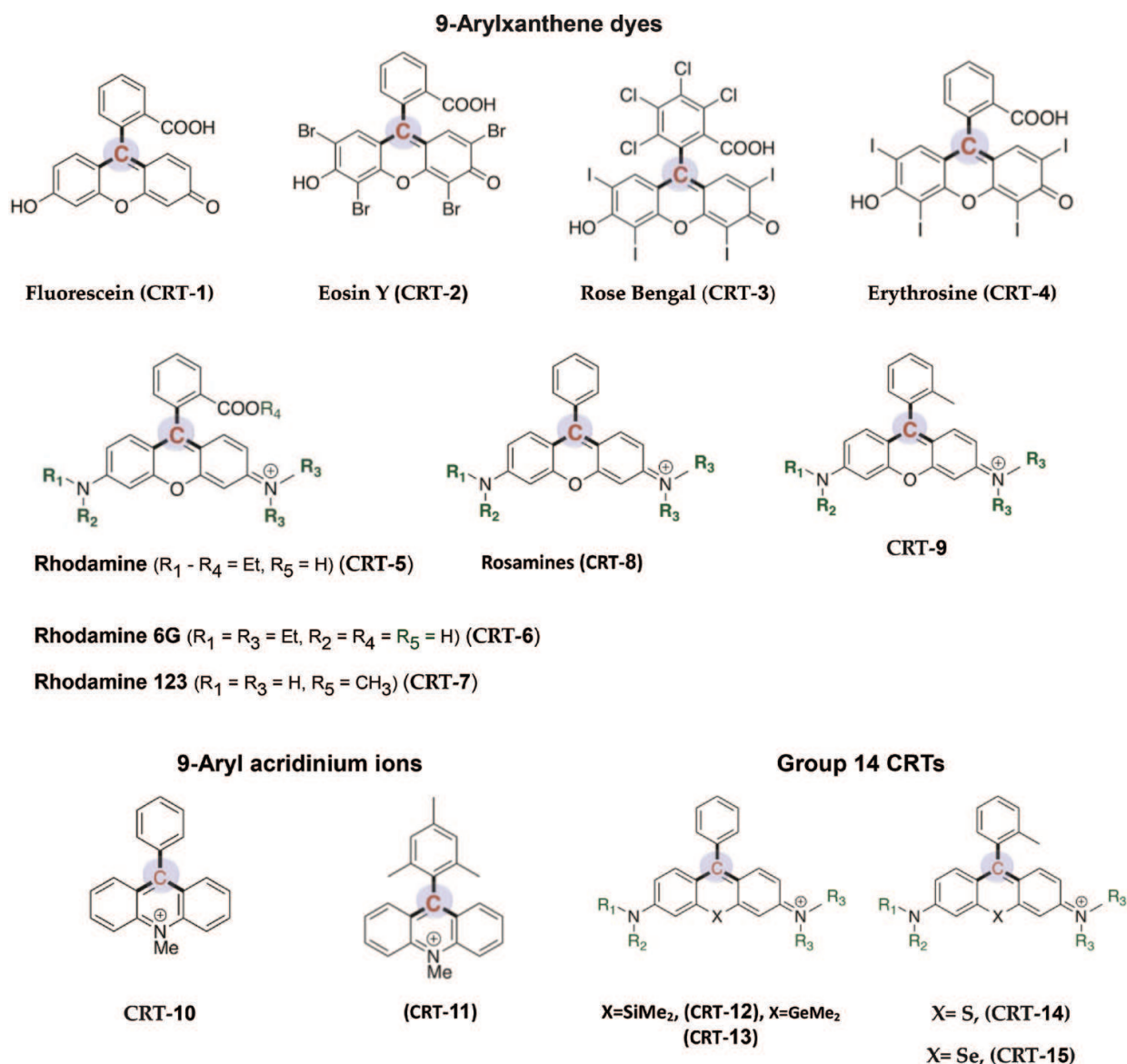
Chart 2. Some common conformationally *restricted* triarylmethanes molecules.

compounds are seldom fluorescent while in cyclic molecules due to the restriction of free rotation in the molecules there is a decrease in the vibrational relaxation through non-radiative pathways and hence there is a increase in the fluorescent quantum yield. To study the effect of this decrement in the conformational freedom and the properties that arise due to this restriction scientists term the molecules with such reduced conformational mobility as "conformationally restricted analogues" [18].

Due to the various non bonded interactions among the ortho protons/substituents in triarylmethanes, the triarylmethanes exhibit 'molecular propeller conformation' in the ground state [17–21]. However, the three aryl rings attached to the central carbon atom rotate freely. This free rotation is restricted as shown in **Figure 2**, on bridging the two aryl rings with heteroatoms or bridging the aryl rings through bonds forming various types of molecules like 9-arylxanthenes (oxygen bridging) [22], 9-arylfluorenes (bridging through C-C bond) [23].
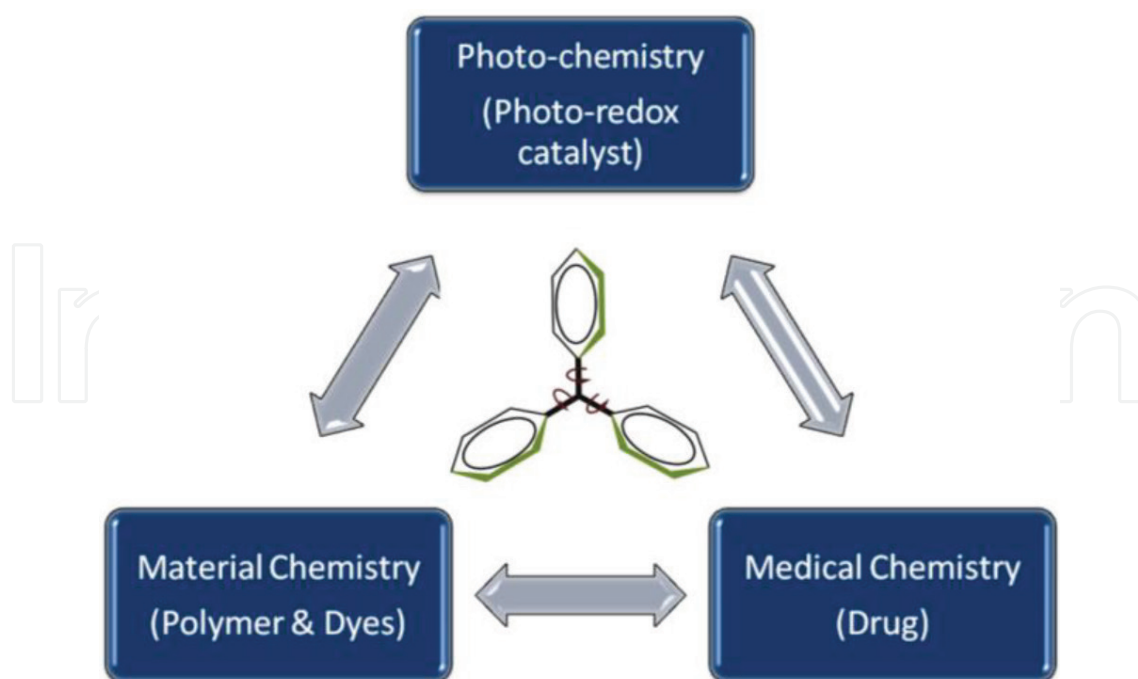
Figure 1. Application of triarylmethane molecular scaffold can be found in various molecular fields.

Figure 2. Restricting conformational flexibility through covalent bonding or bulky substitution to produce CRT molecules.

The presence of three aryl rings as well as the non-fluxional nature of the molecule results in easy abstraction of the corresponding methine hydrogen and thus faster generation of the corresponding free radicals; carbocations as well as carbanions [24]. In fact, Arnett and coworkers have described 9-arylxanthenes (a typical example of CRTs) as a subset of triarylmethanes [25, 26]. Both triarylmethanes, and 9-arylxanthenes are therefore can be considered as amphihydric compounds. These CRT compounds are reported to exist in two forms; one benzenoid and other quinoid structures due to this amphihydric nature as shown in **Figure 3** [27].

This benzenoid and quinoid structures along with the conformational restriction results in various interesting photophysical properties namely, the benzenoid form in the 9-arylxanthene derivatives being colorless while the quinoid form is intensely colored. In the benzenoid form the π electron delocalization in the chromophore is interrupted causing the absorption to be in the ultraviolet region and hence colorless while in the quinoid system this is uninterrupted causing the absorption to be in the visible region and hence is colored [28]. In the presence of base in (**Tram-1**), (**Tram-2**) and their derivatives intramolecular lactonization occur
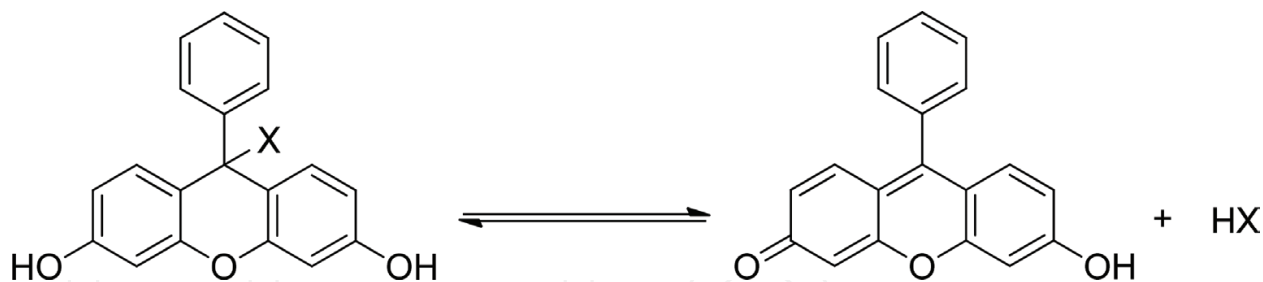
Figure 3. Two structural forms of CRTs.

thus reverting to a benzenoid structure and hence becoming colorless, which has been aptly used to develop various pH indicators as well different dye stuffs [29]. Moreover, in the CRTs, due to the rigid structure, the rate and extent of different relaxation processes involved in the relaxation of the excited molecules to the ground state differs thus showing different fluorescence quantum yield. For example, the CRT molecule (**CRT-1**), displays very high fluorescence (fluorescence quantum yield = 0.92, λ excitation = 485 nm) whereas the corresponding flexible analogue, (**Tram-1**) is almost non-fluorescent [30].

2. Photophysical studies of CRTs: effect of conformational restriction on the photophysical properties

2.1. Photophysics of unrestricted triarylmethanes

The UV–Vis spectrum of the conformationally flexible triarylmethanes are very interesting with predominately two types of absorption bands being observed namely, the x band and the y band as shown (**Figure 4**). The x band arises through the transition of electron from the nonbonding molecular orbital of the molecule to the lowest unoccupied molecular orbital while the y band arises through the transition of the electron from the second highest occupied molecular orbital of the dye to the lowest unoccupied molecular orbital of the dye. This UV–Vis spectrum is found to depend strongly depends on various factors like the structure of the molecule [31–35], concentration [36], pH of the solution [37] as well as temperature [38]. Further due to the conformational flexibility and synchronous rotation among the attached aryl rings, the relaxation of the vibronically excited triarylmethanes to the ground state can occur through various radiation less processes. Due to this vibrational cascading the luminescence intensity and lifetime decrease in conformationally flexible triarylmethanes. However, this vibrational cascading is strongly affected by various factors like concentration, presence of other molecules (proteins/polymers, etc.), pH of the solution, as well as temperature thereby affecting the intensity of various luminescent processes [39].

2.2. Photophysics of conformationally restricted triarylmethanes

Decreasing the synchronous rotation of the aryl rings and hence the conformational flexibility in triarylmethanes has a profound influence in the observed photophysics of the triarylmethanes. The most significant change observed is the increase in the intensity of various luminescence processes. This is due to the fact that on conformational restriction, the relaxation of the excited
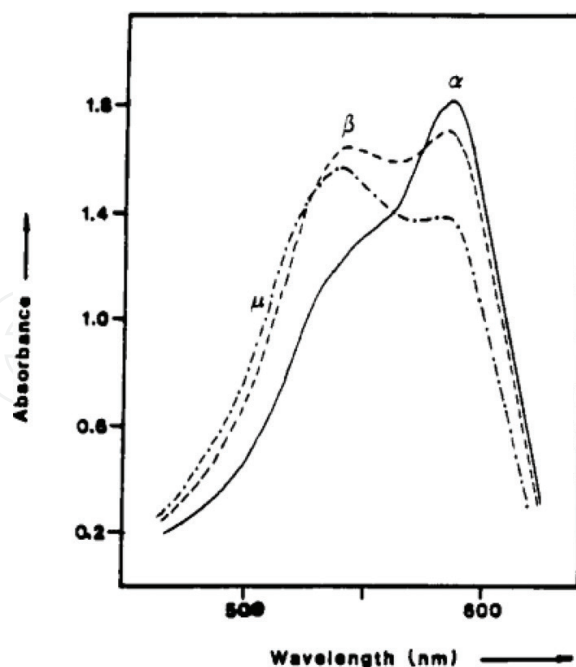
Figure 4. The absorption spectra of triarylmethane (Tram-5) showing the α, β and also the µ band at three different concentrations. Taken from Chem. Rev., 1993, 93, 381 with permissions from American Chemical Society.

state molecule to the ground state through various radiation less transitions decreases causing an increase in the intensity of the various luminescent processes [30]. Furthermore, the rate of the intersystem crossing also increases [40] thereby increasing the population of the triplet state [41].

2.2.1. Effect of structure

The functional groups/ the substituent atoms attached to a molecule modulate the photophysical properties of the molecule to a large extent. For example electron withdrawing groups like nitro groups affects the intramolecular charge transfer processes in the molecule [42], a tertiary amine group increase the rate of relaxation to the ground state through various non-radiative transitions arising due to the rapid rotation around the substituents attached to nitrogen and hence causes a decrease in fluorescence quantum yield [43, 44], heavy atom substituents like iodo, bromo increase the rate of intersystem crossing [45] through efficient spin-orbit coupling decreasing the fluorescence lifetime and quantum yield and concomitantly increasing the triplet emission yield [44].

In the CRTs the substituted aryl rings have a strong influence in the absorption-emission spectra of these compounds. For example depending on the pH of the solution the hydroxy xanthene dyes like (**CRT-1**), (**CRT-2**), (**CRT-3**) and (**CRT-4**), remain either in the protonated form or in the anionic form and the dianionic form. (**Figure 5**) [46], At low pH the protonated form predominates, while at higher pH the anionic form predominates. At still higher pH the dianionic form predominates. In the hydroxy xanthene dyes the emission quantum yield of the protonated form is the lowest while the emission quantum yield of the dianionic form is the highest [47]. Moreover, the greater conjugation observed in the dianionic form causes a red shift in the absorption as well as emission spectra. The intermediate mono anionic species forms a contact ion pair interaction and hence has a blue shift in the absorption-emission spectra [47].
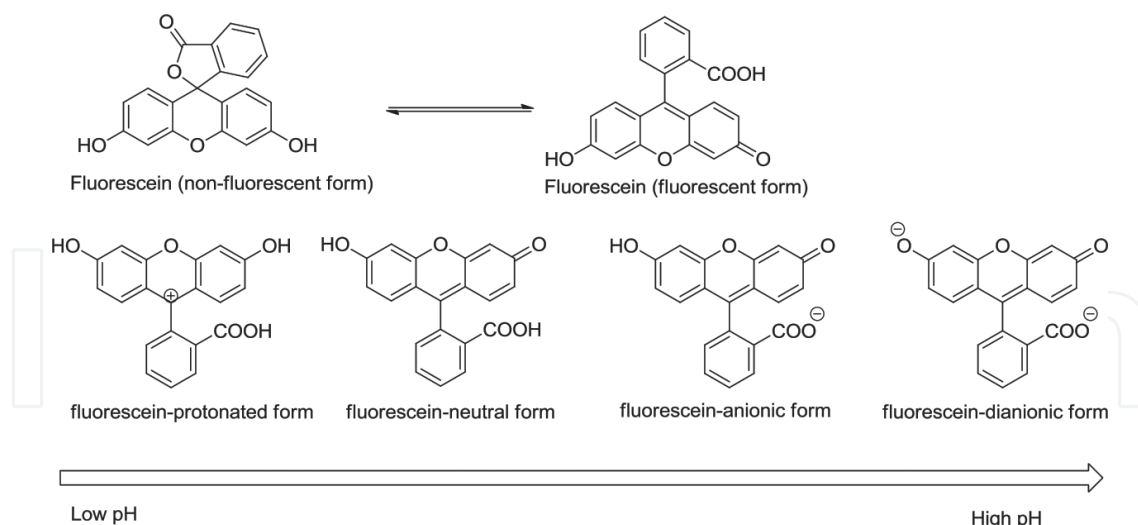
Figure 5. Fluorescent and non-fluorescent form of **CRT-1** at different pH.

2.2.2. Effect of solvent, concentration and temperature

The different structural forms of the hydroxy xanthene dyes have different hydrogen bonding ability with the solvent molecules which is reflected by the change in the UV–Vis absorption spectra on changing the hydrogen bonding ability of the solvent. For example, as observed by Martin and coworkers, with the increase in the hydrogen bonding effect of the solvent both the absorption as well as the fluorescence spectra of hydroxy xanthene dyes shows a blue shift [48]. This is due to the fact that hydrogen bonding interactions between the dye molecule and the solvent stabilizes the ground state of the hydroxy xanthene molecules more than the excited state causing an increase in the HOMO–LUMO energy gap and hence a blue shift in the UV–Vis absorption spectra is observed (**Figure 6**). Also the fluorescence quantum yield of these hydroxy xanthene dyes increase in such hydrogen bonding solvents. Moreover, in polar aprotic solvents in which no solute solvent interaction can take place through hydrogen bonding a red shift in the absorption-emission spectra is observed [49].

The hydrogen bonding interactions between the solute and the solvent molecules also stabilizes the singlet as well as the triplet energy states of the solute molecules with the solvent stabilization energy being most in the singlet ground state of the solute followed by the first excited singlet state. The triplet excited state, is least stabilized through hydrogen bonding. Thus the energy gap between the singlet excited state and the triplet excited state decrease in the hydrogen bonding solvent thereby increasing the rate of intersystem crossing. This interaction also organizes the dye molecules in a particular order changing the distortion required for internal conversion. This influences the rate constants as well as quantum yields for the internal conversion [50, 51].

Various non-covalent interactions between the dye molecule and the solvent as well as between the dye molecules result in the formation of dimer and/or higher order aggregates. These aggregates modulate the absorption-emission spectra CRTs strongly depend on the concentration of the CRT molecules. In fact, at higher concentration, the fluorescence spectra of many CRT molecules like **CRT-1, CRT-2** is self quenched [52]. For example dilute solution of (**CRT-1**) and (**CRT-2**) (concentration less than 5×10^{-5} M) is in the monomer state
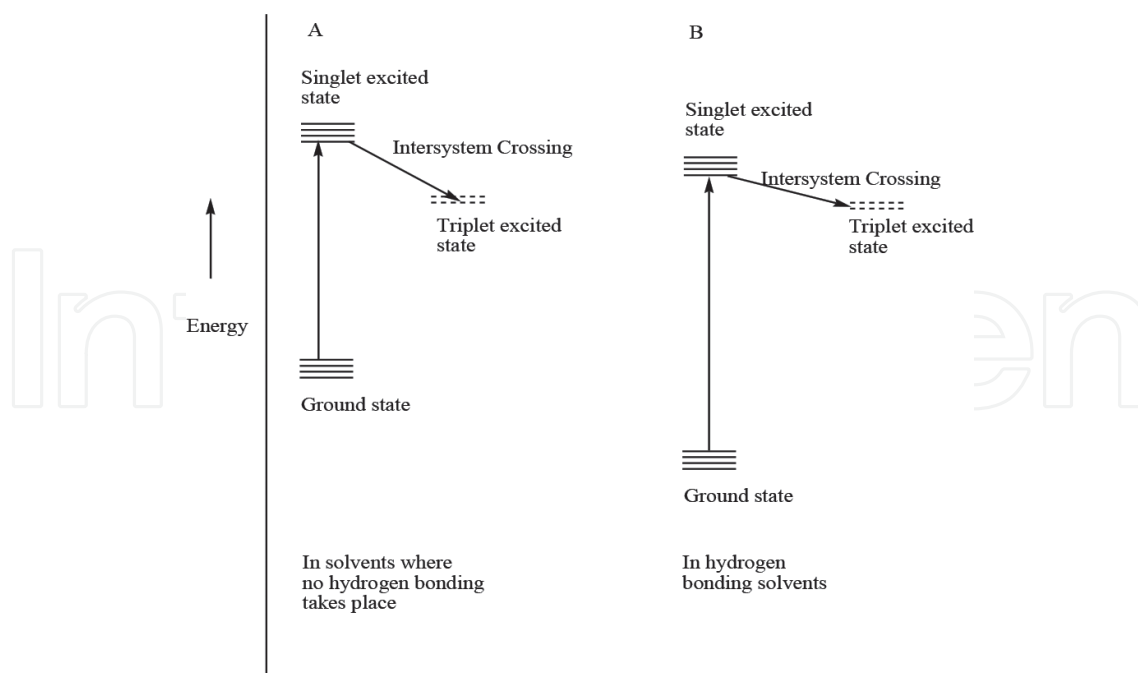
Figure 6. Pictorial representation of the energy levels of (**CRT-1**): (A) in solvents where no hydrogen bonding takes place. (B) In hydrogen bonding solvents. Figure not drawn to scale.

and displays the fluorescence spectra of the monomer form while at concentration range 5×10^{-5} M to 10^{-3} M the fluorescence maxima shifts toward higher wavelength (smaller energy). At very high concentration (above 2×10^{-3} M) with the concentration change there is no change in the fluorescence maxima [52].

Temperature has a profound influence on the fluorescent as well as phosphorescent proper-ties of the CRT molecules [53–56]. This is not only due to the dependence of the population of molecules in a particular electronic state in a molecule depends on the temperature of the molecule (according to Boltzmann distribution factor) but also due to the change in the probability of de-excitation from various vibrational levels through non-radiative transitions changing the fluorescent quantum yield on change in the temperature. Moreover, at low tem-perature, **CRT-5**, **CRT-6**, **CRT-7** show a decrease in the rate of photo degradation showing a strong dependence of the photophysical properties on temperature as shown by Nagano and coworkers [57].
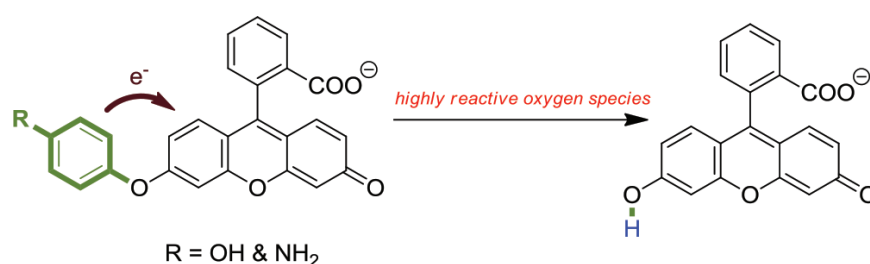
2.2.3. Photoinduced electron transfer (PET) in CRTs

Excitation of molecules from the ground state to the excited state increases the redox activ-ity of the compound. This is due to the fact that on excitation of an electron from the ground state creates an "electron hole" in its highest occupied molecular orbital as well as equivalent amount of electron occupancy in the lowest unoccupied molecular orbital. However, the elec-trons in the LUMO energy level are loosely bound and hence can be easily detached (hence greater reducing ability) while the electron hole in the HOMO results in greater electron affin-ity (hence greater oxidizing ability).

The fluorescence quantum yield of the 9-arylxanthenium ion type of CRT derivatives have been found to be high (fluorescence $\Phi = 0.45$) [53]. However, this high fluorescence quantum yield is effectively quenched in various CRTs molecules having electron-rich aromatic substituents due to a PET from the electron-rich aryl rings to the fluorophore takes place, quenching the observed fluorescence [54]. For example the fluorescence quantum yield of (**CRT-6**) is 0.90 while when the carboxy group of (**CRT-6**) is replaced with an electron donating methyl group (**CRT-9**) the fluorescence quantum yield of the resulting compound reduces to 0.35 [55]. Similarly, the fluorescence quantum yield of (**CRT-1**) is 0.92 while the derivative of (**CRT-1**) formed by adding an electron-rich amino group in the 4′ position has fluorescence quantum yield of 0.015 [56]. This effect has been proved through direct flash photolysis studies as well as through directly isolating the radical/radical ion species. Moreover, this fluorescence quenching strongly depends on the electronic nature of the aromatic donors, the oxidizing potential of the aromatic donors, as well as on the orientation of the electron donors. Thus O-arylated derivatives of (**CRT-1**) have very low fluorescent quantum yield compared to (**CRT-1**) molecules and on oxidizing with highly reactive oxygen species revert back to the (**CRT-1**) molecule thus increasing the fluorescence quantum yield (**Scheme 1**) [57]. However in molecules with electron poor aromatic substituents this photoinduced electron transfer process is shut down due to the electron deficient aryl rings and hence CRTs with electron poor aryl rings has higher fluorescence quantum yield compared to the CRTs with electron-rich substituents. Moreover, due to higher excitation energy of the singlet state the singlet excited state is more oxidizing compared to the triplet excited state [58].

2.2.4. Photophysics of molecules formed through replacement of the bridging atom of CRT with Si atom and other groups 14 and group 16 elements

Molecules formed through the replacement of the bridging heteroatoms in the CRT molecules with Si atom or other groups 14 elements such as Ge, Sn, modulate the energy levels of the parent CRT molecules through various stereoelectronic effects causing a high bathochromic shift in the U.V-Vis absorption spectra. This is because the substituents attached to the group-14 atom has a strong electron pushing inductive effect as well as has a strong σ^*-π^* conjugation between the group 14 atom substituent σ^* orbital and π^* orbital of the fluorophore modulating the HOMO as well as LUMO energy levels. Moreover, this bathochromic shift in the absorption maxima among the group 14 substituted CRTs decreases down the
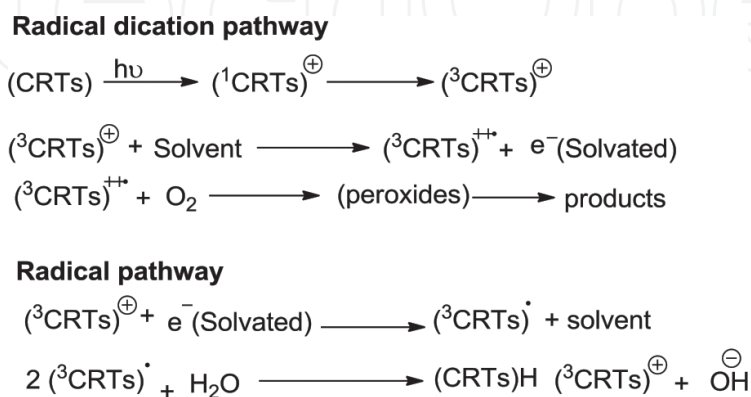

R = OH & NH$_2$

Scheme 1. Photoinduced electron transfer between aryl rings and electron deficient xanthene rings.

group opposite to that observed when the oxygen atom is replaced by group 16 elements. This is due to the fact that in case of group 16 elements the resonance effect takes place between the lone pair of electrons in the chalcogens and the fluorophore with the positive charge being efficiently delocalized throughout the fluorophore resulting in a concomitant decrease in the energy gap between the frontier orbitals. For example, the absorption maxima, fluorescence maxima, fluorescence quantum yield for (**CRT-8**) are respectively 552 nm, 575 nm and 0.84 whereas the same for (**CRT-14**) and (**CRT-15**) formed through the replacement of the bridging oxygen atom with S and Se are 571 nm (λ_{abs} **CRT-14**), 582 nm (λ_{abs} **CRT-15**), 599 nm (λ_f **CRT-14**), 608 nm (λ_f **CRT-15**), 0.44 (Φ_f **CRT-14**) and 0.009 (Φ_f **CRT-15**) respectively. The absorption maxima, fluorescence maxima, fluorescence quantum yield for (**CRT-9**) are 549 nm, 575 nm and 0.35 respectively. For compound (**CRT-12**) and (**CRT-13**) formed through the replacement of the bridging oxygen atom with Si and Ge the absorption maxima, fluorescence maxima and fluorescence quantum yield are 646 nm (λ_{abs} **CRT-12**), 635 nm (λ_{abs} **CRT-13**), 660 nm (λ_f **CRT-12**), 649 nm (λ_f **CRT-13**), 0.31 (Φ_f **CRT-12**) and 0.34 (Φ_f **CRT-13**)respectively [55].

3. Photochemistry of CRTs

3.1. Photooxidation and photoreduction

CTRs with photocleavable appendages dissociate into corresponding cations on irradiation of ultraviolet light. The corresponding ions display a quinoid structure (vide supra, **Figure 2**) and are highly colored. The resulting carbocation takes part in various photooxidation or photoreduction processes. The photooxidation process involves ejection of an electron from the excited state to form the respective triarylmethane carbocation (presumably in the triplet state) which may further react with molecular oxygen to form organic peroxides. It may proceed to further oxidized products or may lose an electron to the solvent molecule to form the respective triarylmethane radical ion or solvated electrons which further reacts with molecular oxygen to form the peroxides (vide **Scheme 2**). The photoreduction process involves either hydrogen atom abstraction or electron abstraction process through a photoexcited triplet state.

Radical dication pathway

$$(CRTs) \xrightarrow{h\upsilon} (^1CRTs)^{\oplus} \longrightarrow (^3CRTs)^{\oplus}$$

$$(^3CRTs)^{\oplus} + Solvent \longrightarrow (^3CRTs)^{++\bullet} + e^-(Solvated)$$

$$(^3CRTs)^{++\bullet} + O_2 \longrightarrow (peroxides) \longrightarrow products$$

Radical pathway

$$(^3CRTs)^{\oplus} + e^-(Solvated) \longrightarrow (^3CRTs)^{\bullet} + solvent$$

$$2\,(^3CRTs)^{\bullet} + H_2O \longrightarrow (CRTs)H\ (^3CRTs)^{\oplus} + \overset{\ominus}{OH}$$

Scheme 2. Different photooxidation processes of CRTs.

3.2. Photoredox catalysis

For practitioners of synthetic chemistry in the pharmaceutical industry, materials industry as well as in the academia the ultimate goal is to develop practical, scalable processes with minimum impact on the environment. On this line, if different sources of energy available to humanity are compared then the light is the most abundant, endless, renewable, clean form of energy and using light to transform raw materials to value-added products will always be of high demand. Moreover, this mode of catalysis provides various new reactions through the facile generation of reactive intermediates which are otherwise difficult/ impossible to obtain. Though transition metal chromophores were used initially as photoredox catalysts, recently organic dyes are being used.

3.3. CRTs as photoredox catalysts

The rich photophysics of CRT derivatives (e.g., facile intersystem crossing due to heavy atom effect, photooxidation, photoreduction, PET, etc.) allow these molecules to be efficiently used as photocatalysts. Especially, the hydroxy xanthene dyes (**CRT-2**), (**CRT-3**), (**CRT-10**) and (**CRT-11**) are noteworthy.

3.3.1. (CRT-2) as a Photoredox catalyst

Due to the heavy atom effect in the (**CRT-2**) molecule, rapid intersystem crossing to the triplet state can take place causing a high triplet quantum yield [59]. Moreover, a photo-induced electron transfer from the benzoate ring to the xanthene fluorophore results in efficient modulation of the redox properties if the dye molecule. The redox potentials of the triplet excited state of (**CRT-2**) indicates that it becomes more oxidizing as well as reducing on photoexcitation, thus photoexcited (**CRT-2**) can act as an electron donor (reducing property) or electron acceptor (oxidizing property) under suitable conditions. Another property of this molecule that is worth mentioning is the fact that due to significant triplet quantum yield (**CRT-2**) can act as triplet energy transfer agent and thus can generate singlet oxygen from air. [60].

3.3.2. Use of (CRT-2) in reduction reactions

##### 3.3.2.1. Nitrobenzene to aniline

Under green light irradiation and in the presence of sacrificial reducing agents like triethanolamine, strong electron acceptors like nitrobenzenes are reduced to aniline derivatives (**Scheme 3**) [61]. Through flash photolysis experiments the mechanism of the reaction was established. (**CRT-2**) loses an electron to the strong electron acceptor nitro group which is converted to the intermediate radical anion. The photocatalyst returns to the ground state through an electron acceptance from the sacrificial reductant triethanolamine which is converted to the aminyl radical cation. This radical cation intermediate then reduces the nitro intermediate radical anion to aniline derivative.

Scheme 3. (CRT-2) catalyzed photoredox conversion of nitrobenzene to aniline.

3.3.2.2. Desulfonylation

A metal-free green protocol for the removal of sulfonyl group was reported by Wu and coworkers (Scheme 4) [62]. Blue light irradiation to bis tetrabutylammonium (CRT-2) salt excites it to its excited state which is oxidatively quenched by β-arylketosulfones resulting the (CRT-2) radical cation and the radical anion of β-arylketosulfones which then undergoes desulfonylation to the aryl ketone radical. The sacrificial reductant closes the catalytic cycle by reducing the (CRT-2) radical cation to (CRT-2) photocatalyst and its radical cation which releases a hydrogen atom to the ketone radical.
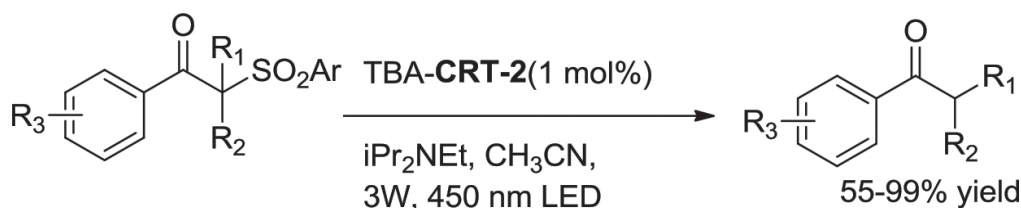

Scheme 4. Reductive desulfonylation of β-keto sulfones catalyzed by CRT2.

### 3.3.3. Use of (CRT-2) in oxidation reactions

3.3.3.1. Benzylic oxidations

In a formal Kornblum oxidation, when benzyl bromides are heated at 80°C in the presence of (CRT-2) as the photocatalyst in the presence of oxygen in DMSO solvent moderate to high amount of arylaldehydes are formed (Scheme 5) [63]. However, interestingly, benzyl chlorides were inert to this oxidation reaction. Moreover, both oxygen, as well as DMSO, was found to be essential for the success of the reaction.
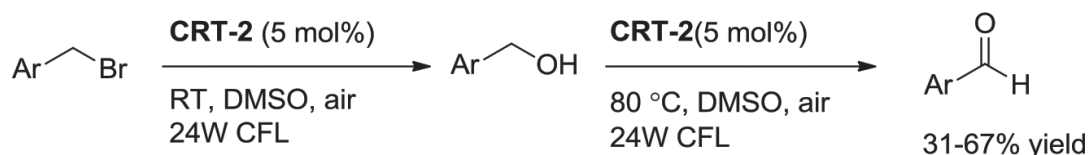
Scheme 5. (CRT-2) catalyzed conversion of benzyl bromides to benzaldehydes.

3.3.3.2. Oxidative iminium ion formation

Single electron transfer from tertiary amines to the excited state of the (**CRT-2**) leads to the formation of aminyl radical cation and the radical anion of eosin. The radical anion of (**CRT-2**) further loses an electron to oxygen molecule to form the reactive superoxide radical anion which further abstracts a proton from the aminyl radical cation to form the imine intermediate resulting in the oxidative imminium ion formation [64]. The high electrophilicity of the iminium ion can be further exploited for the efficient construction of C-C and C-P bonds by treating the formed iminium ions with the nucleophilic partners like indole, dialkyl malonates, dialkyl phosphonates, etc. (**Scheme 6**).

HNu = Nitromethane, Diethylmalonate,
Diethyl phosphonate, etc.
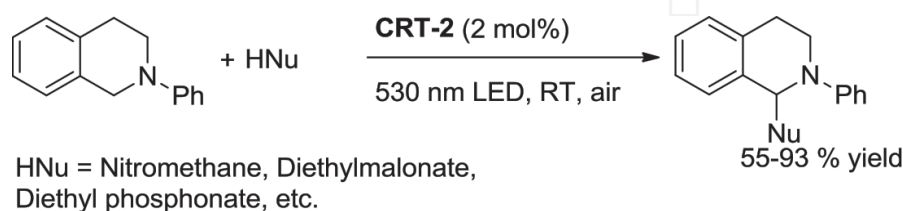
Scheme 6. C-C and C-P bond formation through oxidative iminium ion formation.

3.3.3.3. Benzylic bromination

Using carbon tetrabromide as an efficient source of bromine, morpholine as a reducing agent and (**CRT-2**) as a photocatalyst, Tan and coworkers developed an efficient process for the selective bromination of aliphatic and benzylic C-H bonds (**Scheme 7**) [65]. The authors suggested an intermediate formation of N-morpholino radical for the crucial C-H functionalization step.
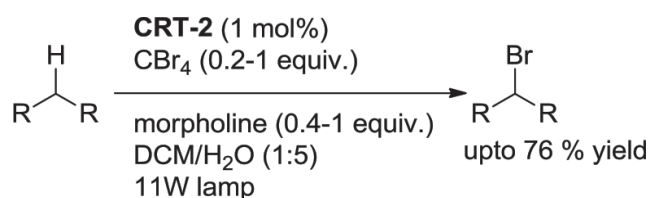

Scheme 7. Photoredox C-H bromination of alkanes catlyzed by (**CRT-2**).

3.3.4. Use of (CRT-2) in redox neutral transformation

3.3.4.1. Arylation reaction using aryldiazonium salts

Excited (**CRT-2**) molecules take part in a SET with aryldiazonium ions to form aryl radicals and (**CRT-2**) radical cation. The formed aryl radical then adds to the double bond of the heteroarenes to form the corresponding radical intermediate which further undergoes a SET to either the (**CRT-2**) radical cation to close the catalytic cycle or to the aryldiazonium ions to form aryl radicals. The corresponding carbocations so formed further aromatizes to give the C-H arylated product. Thus aryldiazonium salts can be used as a source of aryl radicals for redox neutral arylation (**Scheme 8**).
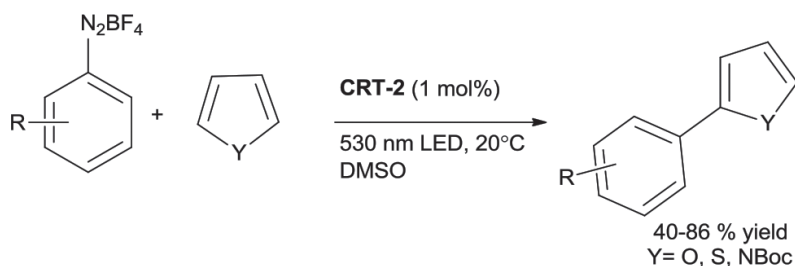
Scheme 8. Redox neutral arylation of heteroarenes.

3.3.4.2. (CRT-11) as photoredox catalyst

The, (**CRT-11**) a class of triarylmethane derivatives, with electron-rich aryl rings in the 9th position, display a unique ability to form a donor-acceptor type of dyad where the electron-rich aromatic ring acts as electron donor while the acridinium ring acts as an electron acceptor. Moreover, the presence of sterically hindered aryl group in the 9th position shields the benzylic position from any nucleophilic attack and also shifts the absorption maxima to the visible range through electron delocalization with the aryl ring. When irradiated with light of suitable frequency (approx. 450 nm absorption maxima) an intramolecular electron transfer from the electron-rich aromatic nucleus to the singlet excited state of the acridinium ring takes place (PET) leading to the formation of the long lived electron transfer excited state. As evident from the reduction potential of the excited state of this molecule, this molecule can easily accept electrons to oxidize organic substrates to its radical cations which can further react with nucleophiles to form the radical adducts while the dye molecule itself loses electrons to electron acceptors like oxygen to form hydroperoxide radical. This radical may further react with the adduct to form its hydroperoxide and further to its oxidized species and hydrogen peroxide (**Figure 7**). Thus in the presence of air (**CRT-11**) can act as an efficient oxidizing agent reducing oxygen molecule (in air) to hydrogen peroxide [13]. For example, this class of dyes has been
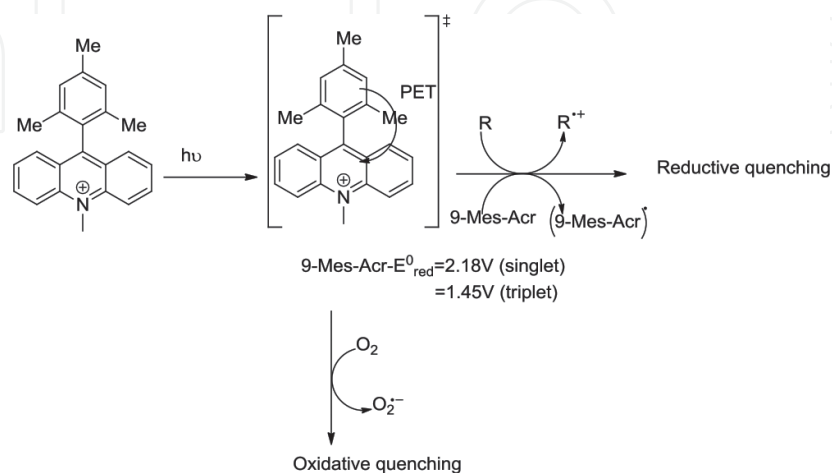

Figure 7. PET, reduction potential, reductive quenching and oxidative quenching of 9-Mes acridinium ions.

effective photocatalysts in the oxygenation of aromatic hydrocarbons to aromatic aldehydes, in C-H oxidation of cycloalkanes and also in the alkene hydrofunctionalization.

3.3.4.3. Use of 9-Mes acridinium ions as oxidizing agent

3.3.4.3.1. Oxidation of toluene to benzaldehyde

In the presence of (**CRT-11**) as photocatalyst and under oxygen atmosphere methyl arenes are converted to their respective aldehydes in high yields (**Scheme 9**) [66]. Remarkably in substrates with multiple methyl groups only single methyl group is oxidized thus showing high selectivity of the method. The acridinium photocatalyst oxidizes the arenes to the corresponding arene radical cation, which further yields a benzylic radical through loss of a proton. Aerial oxygen may oxidize the benzyl radical to peroxyl radical which disproportionate to the observed product. A SET from the oxygen molecule regenerates the acridinium ion catalyst to the ground state.
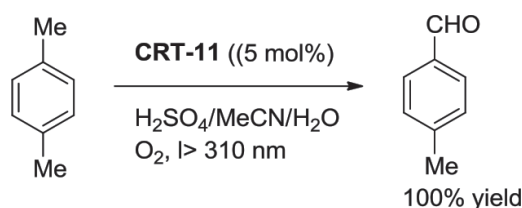
Scheme 9. Selective oxidation of p-xylene to p-tolualdehyde.

#### 3.3.4.3.2. C-H oxidation of cycloalkanes

Fukuzumi and coworkers reported a photocatalytic process to oxidize the inert C-H bonds of cycloalkanes [67]. Using the photoredox catalyst (**CRT-11**) in the presence of oxygen and hydrochloric acid a mixture of cycloalkanols and ketones could be obtained (**Scheme 10**). Though low yields of the product were obtained, the high TON could be achieved. Moreover, the ability to functionalize an inert C-H bond is the utility of the process. The mechanism of the reaction involves oxidation of the chloride ions to chlorine radicals which abstract a hydrogen atom from the C-H bond of the cycloalkanes to form the alkyl radical. The alkyl radical reacts with oxygen to form alkyl peroxyl radical which disproportionate to the products. The involvement of the alkyl peroxyl radical is determined through EPR spectra.
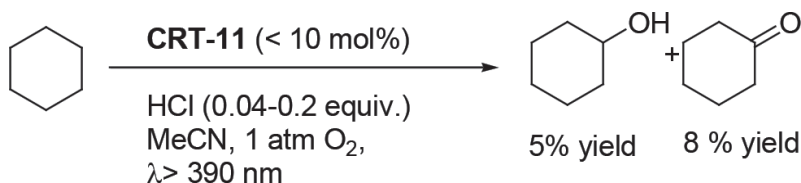
Scheme 10. Photoredox C-H oxidation of cycloalkanes.

3.3.4.4. Use of (CRT-11) for alkene hydrofunctionalization reaction

The regioselective alkene hydrofunctionalization is an essential yet challenging task in synthetic chemistry. Nicewicz developed an efficient protocol for alkene hydrofunctionalization using the (**CRT-11**) as the photocatalyst (**Scheme 11**) [68–70]. Thus in the presence of (**CRT-11**) alkenes can be oxidized to their corresponding radical cations, which react with the nucleophiles at the less substituted position to produce the more stable nucleophile cation radical adduct thus giving rise to the observed regioselectivity. Further, a HAT from added HAT to the produced radical gives the observed product and the corresponding radical of the HAT agent. This radical then regenerates the (**CRT-11**) ions catalyst in the ground state, the HAT agent being converted to its anion. The so produced anion of the HAT agent deprotonates the nucleophile cation radical adducts to regenerate the HAT agent. This transformation allows efficient construction of C-C, C-O, C-N, etc. bonds through the use of nucleophilic arenes, carboxylic acids, alcohols and amines. Of special note is the fact that through the use of photoredox catalyst, addition of hydrochloric acid can take place in anti Markovnikov fashion.
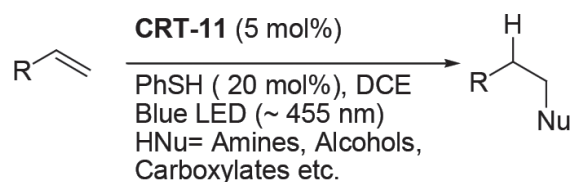
Scheme 11. (**CRT-11**) catalyzed alkene hydrofunctionalization.

4. Conclusion

The free rotation among the three aryl rings of the triarylmethane molecule is restricted on bridging the aryl rings with heteroatoms or through bonds. The resulting conformationally restricted triarylmethane molecules have very rich photophysics which is the topic of this chapter. This conformational restriction decreases the rate of relaxation of the excited molecules through vibrational cascading increasing the fluorescent intensity of the resulting compound. Heavy atom substituted CRTs shown a high rate of intersystem crossing thus increasing the triplet quantum yield and also gives rise to unique photochemistry which is discussed. This property is used currently to develop small organic molecules catalyzing the conversion of light energy to value-added products which is also discussed. We anticipate that this chapter will benefit readers interested to develop novel photocatalytic systems to synthesis various value-added products.

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Conflict of interest

The authors declare no conflict of interest.

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