Indian Journal of Chemistry
Vol. 62, October 2023, pp. 1047-1055
DOI: 10.56042/ijc.v62i10.6183

Photophysical and singlet oxygen generation studies of a few water soluble triazatriangulenium salts

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Received 1 October 2022; accepted (revised) 17 August 2023

The photophysical and singlet oxygen generation studies of a few water-soluble triazatriangulenium cations (TATA) are reported. The photophysical studies include absorption spectrum, fluorescence spectrum, fluorescence quantum yield, fluorescence lifetime, triplet life time, triplet quantum yield and phosphorescence spectrum. The singlet and triplet energy levels of the compounds were determined. The triplet state properties have been characterized using nanosecond laser flash photolysis studies. The singlet oxygen generation has been estimated using chemical actinometry using disodium-9,10-anthracenedipropionic acid in water and 1,3-diphenylisobenzofuran in acetonitrile as the chemical actinometers and rose bengal was used as reference.

Keywords: Triangulenium cations, Singlet oxygen, Thermally assisted delayed fluorescence, Disodium-9,10-anthracene dipropionic acid, 1,3-Diphenylisobenzofuran

The exceptionally stable triangulenium cations have caught attention in the various areas of scientific research. Over the last two decades, these compounds found use in supramolecular assemblies[1-5], and can act as chiral platforms[6,7]. Researchers attention to this class of compounds gained because of their wide range of biological[8-11], chemical[12-14], photochemical/ photophysical[15-23], stereochemical[6,24], structural[24-27], supramolecular[28,29], and synthetic[30] properties. The first member in this group is trioxatriangulenium ion [$TOTA^+$] reported by Martin and Smith in 1964 (Ref. 31). $TOTA^+$ is far less susceptible to nucleophilic attack because of the extensive delocalization of the lone pairs on the three oxygen atoms in the ground state[32]. High pK_{R+} value of $TOTA^+$ (9.05) is an indication of its exceptional stability in aqueous medium. Johannes Reynisson *et al*. have shown that $TOTA^+$ binds with duplex DNA with a preference for GC base pairs[33]. They also reported its photophysical properties and electrophilic reactivity in the ground state and excited singlet state[19]. On changing the bridge oxygen atoms in $TOTA^+$ with nitrogen atom resulted in the highly stable triazatriangulenium salts with pK_{R+} value 23.7 (Ref. 13). This group has reported some triazatriangulenium salts having different alkyl chains on the bridging nitrogen atom. In the same period, Dileesh and Gopidas studied and reported the photoinduced electron transfer properties of azatriangulenium salts[20]. They found that the mono-aza derivative act as an excited state electron acceptor but replacement of oxygen atoms with nitrogen leads to a gradual shift of photoinduced electron transfer property from an acceptor to that of a donor. Cyril Nicolas *et al*. reported the use of these azatriangulenium salts as phase transfer catalysts for several organic reactions[30]. The extreme stability in basic and nucleophilic conditions makes them a suitable candidate for phase transfer catalysis. Solubility is a criterion for many applications, especially for biological applications. Hitherto known triangulenium cations are insoluble in aqueous medium and their use as a dye in biological applications are absent. A strategy to improve aqueous solubility is to introduce polar groups on the framework of the molecule or as substituents on the

alkyl chain. We succeeded in getting a series of water-soluble triazatraingulenium cations by utilizing the known synthesis methods. The present paper discusses the synthesis and photophysical properties of a series of water-soluble triazatriangulenium salts with a focus on their photosensitized singlet oxygen generation properties (Scheme 1). Such visible light absorbing molecules with exceptional thermal and photochemical stabilities find use in photodynamic applications. Here, the singlet oxygen generated could be used for photoremediation of contaminated water or as a potential drug candidate for photodynamic therapy. The singlet oxygen sensitization ability of these compounds were assessed by determining the apparent singlet oxygen quantum yields using 9,10-anthracene dipropionic acid in water and 1,3-diphenylisobenzofuran in acetonitrile as the chemical actinometer and rose bengal as the reference sensitizer.

Experimental Section

Solvents used were of reagent grade and used without further purification. Reagents were purchased from Sigma-Aldrich and used as received. Absorption spectra were recorded using Evolution 201 UV-Vis spectrophotometer. Fluorescence, phosphorescence and fluorescence lifetime measurements were carried out using JobinYvon Fluorolog 3-211 UV-Vis-NIR fluorescence spectrometer. IR spectra were recorded on JASCO 4100 model, FTIR spectrometer. The ^{1}H NMR spectra were recorded at 400 MHz on Bruker FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Molecular mass was determined by Waters 3100 mass detector with an Electro-Spray-Ionization unit. Fluorescence quantum yields were determined using Rhodamine 6G as the reference. Laser flash photolysis experiments were carried out by employing an Applied Photophysics model LKS-20 laser kinetic spectrometer equipped with a GCR-12 Series Quanta Ray Nd:YAG laser. The analysing and laser beams were fixed at right angles to each other. The laser energy was 60 mJ at 355 nm. For quantum yield measurements optically matched solution of Tris(2,2'-bipyridine) Ruthenium (II) in acetonitrile were used as reference (R). Values of $\Phi_T^R = 0.95$ and ε_T^R = 27300 M^{-1} cm^{-1} at 370 nm were used in the calculation[34]. Singlet oxygen quantum yield was monitored by chemical actinometric method using 9,10-anthracenediprop ionic acid and 1,3-diphenylisobenzofuran as the chemical actinometer in water and acetonitrile respectively and rose bengal as standard.

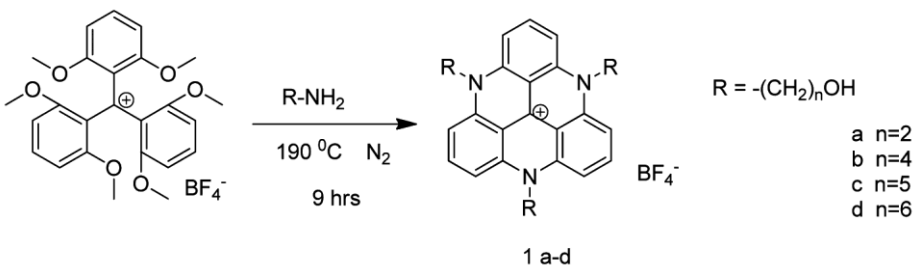
Tris(2,6-di-methoxyphenyl)carbenium tetrafluroborate was prepared based on the reported procedure[31]. Compounds **1a-d** were prepared by mixing Tris(2,6-di-methoxyphenyl)carbenium tetrafluroborate with appropriate amino compounds and heated to 190°C under nitrogen atmosphere for 9 h. The resulting solid was then triturated several times with dichloromethane and hexane. Selective crystallization occurred from methanol to give corresponding triazatriangulenium derivatives.

Results and Discussion

Photophysical properties

Absorption and emission properties

The absorption and emission properties of **1a-d** in acetonitrile and water are summarized in Table 1. Absorption spectra of the tri-N-alkyl triazatriang ulenium salts in acetonitrile were reported earlier by Laursen and Krebs[13]. The cations **1a-d** also showed similar spectral properties in acetonitrile and water. But in saline water (0.1 M NaCl) the spectrum is red shifted by 5 nm than in acetonitrile, with a shoulder band at 505 nm. The spectral studies as a function concentration of **1a-d** do not show any change in spectral profile thus by ruling out the chance of aggregations of the dyes. Since all the spectral features of compound **1a-d** are similar, in this paper we will be focusing on the photophysical studies of **1a** only. Fig. 1 is a comparison of UV-Vis absorption of



1 a-d

Scheme 1

Table 1 — The absorption maxima λ_{max}(Abs),extinction coefficients(ε_{max}),emission maxima(λ_{max}(Em)nm),fluorescence quantum yields($\Phi_{f)}$,fluorescence lifetimes (τ) and radiative and non radiative rate constant for triazatriangulenium salts 1a-d in water. Values given in parentheses are those in acetonitrile.

Compd	λ_{max}(Abs) nm	$\varepsilon_{maxM}{}^{-1}{}_{cm}{}^{-1}$(log ε)	λ_{max}(Em) nm	Φ_F	τ_F (ns)	$k_r(s^{-1}) \times 10^{-2}$	$k_{nr}(s^{-1}) \times 10^{-2}$
1a	530 (525)	4.6 (5)	571 (558)	0.15 (0.20)	11 (8.1)	1.36 (2.46)	7.72 (9.8)
1b	530 (525)	4.6 (5)	571 (558)	0.15 (0.20)	10.9 (8.1)	1.37 (2.46)	7.79 (9.8)
1c	530 (525)	4.6 (5)	571 (558)	0.15 (0.20)	10.5 (8.2)	1.42 (2.43)	8.09 (9.7)
1d	530 (525)	4.6 (5)	571 (558)	0.15 (0.20)	10.5 (8.1)	1.42 (2.46)	8.09 (9.8)

compound **1a** in acetonitrile and water respectively.

The fluorescence spectra of tri-N-alkyltriazatria ngulenium salts in acetonitrile solution were reported earlier by Dileesh and Gopidas[20]. Fig. 2 shows the comparison of fluorescence spectra of these compounds in acetonitrile and water (0.1M NaCl). In water, the emission spectra of all these compounds are red shifted by 13 nm in comparison to those observed in acetonitrile.

Phosphorescence spectra of triazatriangulenium cation

The compounds **1a-d** exhibited the phosphorescence at 77 K in ethanol glass with an emission maximum at 563 nm. The phosphorescence spectrum obtained for **1a** at 50 µs delay after the excitation flash in ethanol glass at 77 K is given in Fig. 3.

Thermally Assisted Delayed Fluorescence (TADF) in triazatriangulenium cations

The singlet state energy for the compounds **1a** was estimated from the point of intersection of the normalized absorption and fluorescence spectra and the value obtained was 53 kcal M^{-1}. The triplet energy of 49.72 kcal M^{-1} was estimated from the point of intersection between the normalized excitation and phosphorescence spectra.

The small singlet – triplet energy gap(3.28 kcal M^{-1}) can cause thermally assisted reverse intersystem crossing between triplet and singlet states leading to the observation of a delayed fluorescence emission. The compounds **1a** showed delayed emission both in acetonitrile and water. The fluorescence emission spectrum under inert condition shows fourfold enhancement in the intensity compared to oxygen saturated solutions. This is because of the quenching of a fraction of the triplet states of **1a** by oxygen

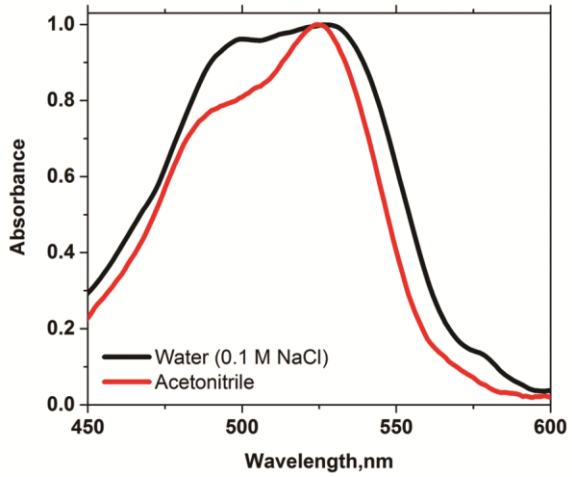


Fig. 1 — Normalized emission spectra of **1a** in water (—) and acetonitrile (—)

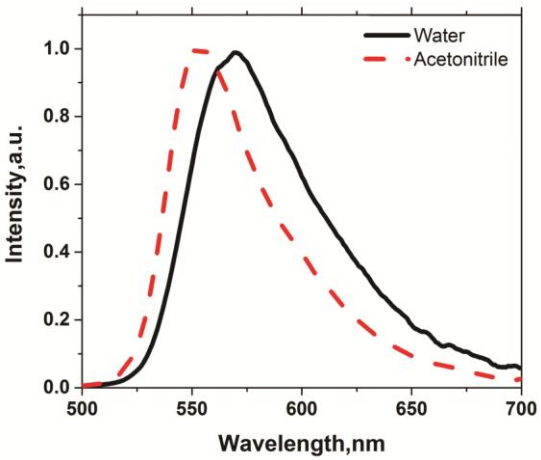


Fig. 2 — Normalized emission spectra of **1a** in water (—) and acetonitrile (- - -). Excitation wavelength was 480 nm

leading to a reduction of triplet excited state population. Thus the number of molecules undergoing thermally activated reverse intersystem crossing decreases, resulting in a reduced intensity of the delayed emission. This is shown as Fig. 4a and

Fig. 4b in acetonitrile and water respectively. The emission decay profile was also recorded after an initial delay of 25 µs for nitrogen saturated and air saturated solutions of **1a** in acetonitrle and water. Both decays gave good fit to a single exponential function and obtained emission lifetimes as 15 µs and 4 µs respectively for the nitrogen saturated and air saturated solutions. The value obtained in the absence of air is very close to the value of triplet lifetime obtained for the same compound in water in the absence of oxygen.

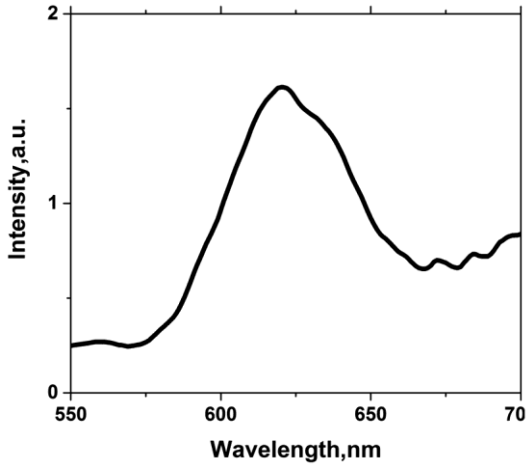


Fig. 3 — Phosphorescence spectrum of **1a** in ethanol glass at 77 K

Laser flash photolysis studies

Laser flash photolysis studies of **1a** in acetonitrile and water saturated with argon led to the formation of transients characterized by absorption at 370 nm, 420 nm and 650 nm with a bleaching in the 450-600 nm region. Representative example of the transient absorption spectra recorded in water (0.1 M NaCl) and acetonitrile at various time intervals after the laser pulse is given in Fig. 5. The values of the absorption maxima are given in Table 2.

The transients in all these cases decayed with first order kinetics and the decays are independent of the concentration of **1a** avoiding the chance of self quenching. The life time of the transients are listed in Table 2. The transients from all these compounds were quenched by oxygen. Hence we assign these

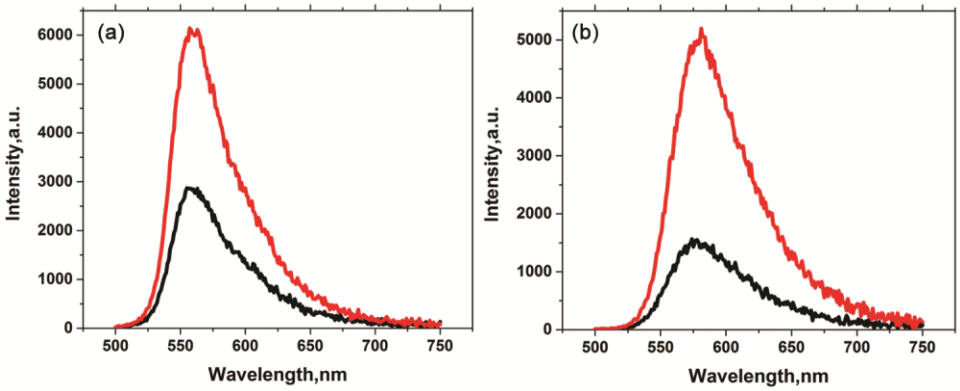


Fig. 4 — (a) Delayed emission observed for **1a** in air saturated (—) and nitrogen saturated solution in acetonitrile (—) (b) in air saturated (—) and nitrogen saturated solution in water (0.1 M NaCl) (—).

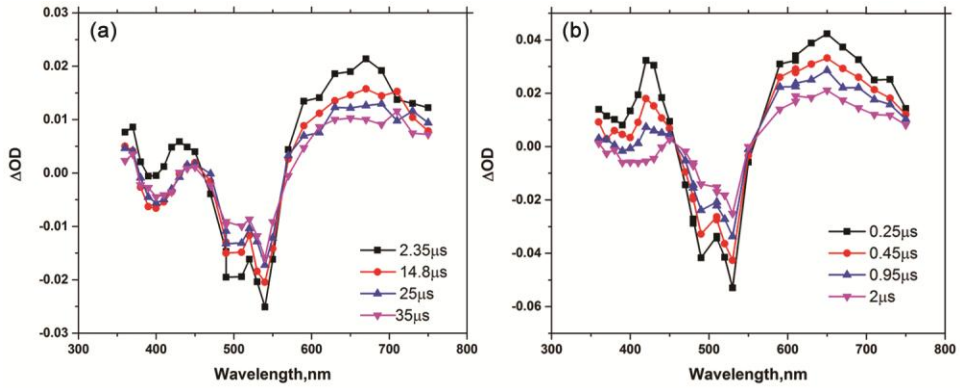


Fig. 5 — The transient absorption spectrum of **1a** in water (0.1 M NaCl) acetonitrile recorded with different time delays after laser excitation (λ_{ex}=532 nm)

Table 2 — Triplet-triplet absorption maxima (λ^{T}_{max}(Abs)), extinction coefficients ($\acute{\varepsilon}^{T}_{max}$), triplet quantum yield(Φ_T), triplet lifetime (τ_T), triplet energy (E_T), oxygen quenching rate constant (kq(O_2)) for triazatriangulenium salts in water. Values given in parenthesis are those recorded in acetonitrile.

Compd	λ^{T}_{max}(abs) (nm)	ε^{T}_{max}(abs) M^{-1} cm^{-1}	Φ_T	τ_T μs	E_T eV	kq(O_2) M^{-1} s^{-1}
1a	650 (650)	5.43×10^3 (8.0×10^3)	0.68 (0.64)	21.6 (1.85)	2.11 (2.11)	1.41×10^7 (1.9×10^6)
1b	650 (650)	5.45×10^3 (8.1×10^3)	0.68 (0.64)	27.2 (1.52)	2.11 (2.11)	1.43×10^7 (1.9×10^6)
1c	650 (650)	5.43×10^3 (8.1×10^3)	0.68 (0.64)	21.6 (1.67)	2.11 (2.11)	1.41×10^7 (1.9×10^6)
1d	650 (650)	5.42×10^3 (8.1×10^3)	0.68 (0.64)	27.3 (1.95)	2.11 (2.11)	1.42×10^7 (1.9×10^6)

transients as triplets of these substrates. We have determined oxygen quenching rate constants $k_q(O_2)$ in all the cases and these values are reported in Table 2. Since all the transient absorption spectra obtained in acetonitrile and water showed strong bleaching in the region of the ground state absorption, the extinction coefficients of the triplet absorptions by the singlet depletion method[34]. This method assumes that the triplet does not absorb in the region of the depletion. The values of the extinction coefficients are reported in Table 2. Using these extinction coefficients, we have determined the triplet quantum yields Φ_T for all the substrates by the relative actinometry method[35]. The values thus obtained are given Table 2.

Laser flash photolysis studies: Triplet quenching experiments

The quenching of the triplet by the oxygen was attempted by laser flash photolysis. The triplet quenching rate constants were obtained by plotting pseudo-first-order rate constants (K_{obs}) against different quencher concentrations [Q] and using equation 1

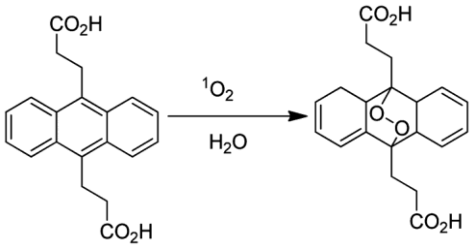
$$K_{obs} = K_0 + K^{T}_{q}[Q] \quad \ldots (1)]$$

Where K_0 (= $1/\tau_0$) is the decay rate in the absence of any quencher. Stern-Volmer plots are drawn for the compounds to determine the oxygen quenching rate constants in water and acetonitrile. The oxygen quenching rate constants are tabulated in Table 2.

Singlet oxygen generation studies

Singlet oxygen quantum yield in water

The singlet oxygen quantum yield, Φ_Δ was measured using Chemical Actinometer method. Since the present study uses aqueous medium we have used water soluble actinometer disodium 9,10-anthracenedipropionic acid (ADPA). The use of ADPA in the detection of $^1O_2$ was first described by Lindig *et al*.[36] The anthracene structural unit in ADPA reacts with singlet oxygen in a [4+2] cycloaddition reaction to produce an endoperoxide[37] (Scheme 2).



Scheme 2

The endoperoxide does not have absorbance in the 350 to 400 nm region where ADPA absorbs and the endoperoxide is thermally stable at RT. It is a useful method of quantification as, even when $^1O_2$ generation rates are low, the concentration of endoperoxide produced remains proportional to the cumulative amount of $^1O_2$ generated[38]. The rate constant for reaction with $^1O_2$ (Ref. 39) and high-water solubility, makes ADPA a very efficient singlet oxygen scavenger in aqueous media and in systems with biological applications. The irradiation wavelength selected for the actinometry was 530 nm and the medium used was a saline buffer solution with a *p*H 7. The actinometer did not have any absorption at the wavelength of irradiation. The irradiation was performed with a ultra bright green LED bulb and the incident photon rate is calculated as $9.5\,(\pm0.5)\times10^{16}$ photons s^{-1} using chemical actinometry. Aberchrome 670 was used as the chemical actinometer. In the presence of ADPA $^1O_2$

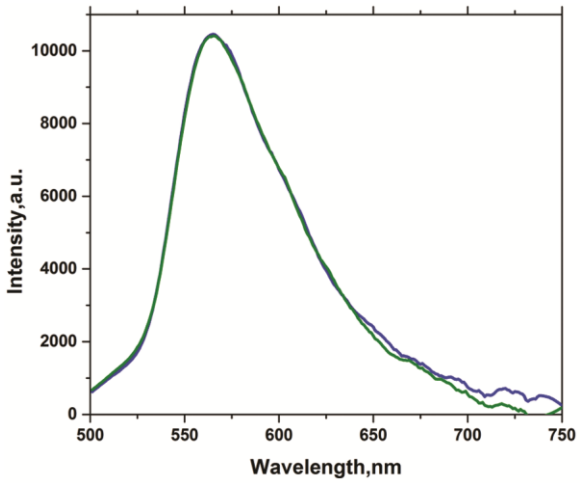


Fig. 6 — Emission spectrum of **1a** (1.0×10^{-6}M) in water in the presence of increasing concentrations of ADPA (1.4×10^{-4}M - 2.6×10^{-4}M)

generated by a sensitizer S undergoes the following decay processes in solvent[44].

(i) Light absorption by the sensitizer:
$^1S + h\tilde{o} \longrightarrow {}^1S^*$

(ii) Intersystem crossing:
$^1S^* \longrightarrow {}^3S^*$

(iii) Energy transfer:
$^3O_1 + {}^3S^* \longrightarrow {}^1O_2 + {}^1S$

(iv) Singlet oxygen deactivation by the solvent $^1O_2 \longrightarrow {}^3O_2$

(v) Physical quenching of $^1O_2$ by ADPA
$^1O_2 + ADPA \longrightarrow ADPA + {}^3O_2$

(vi) ADPA oxidation by $^1O_2$

(vii) $^1O_2 + ADPA \longrightarrow ADPAO_2$

To understand whether ADPA interferes with the excited state of triazatriangulenium salts **1a**, the emission spectra were recorded at various ADPA concentrations. It is shown in Fig. 6.

A blank irradiation of ADPA in the absence of the sensitizer **1a** was carried out which did not show any change in the concentration of ADPA, indicating its high photostability. As expected a decrease in the absorbance in the range of absorption spectrum of a mixture of dye and ADPA upon irradiation at 530 nm was observed. This helped us to monitor the reaction making use of UV-Vis spectroscopy as a tool. The rate of consumption of singlet oxygen by ADPA can be calculated in the presence of the triangulenium dye (**1a**) as well as the reference sensitizer rose bengal. Since there was no change in the emission spectrum of **1a** at various concentrations of ADPA (Fig. 6), it ruled out the excited state interactions of **1a** and ADPA. It was noted that ratio of rate constants for the photobleaching of dye and the reference sensitizer was found to be proportional to their ratios of singlet oxygen generation efficiency. Rose bengal has a singlet oxygen quantum yield of 0.76 in water[40]. From these data the apparent quantum yield of singlet oxygen generation could be estimated. An air saturated aqueous solution of ADPA (1.8×10^{-4}M) is irradiated in the presence of the triazatriangulenium salt (1.6×10^{-4}M) using ultra bright green LED. For total absorption of the incident light the absorbance at the irradiation wavelength was ensured to be above 2 absorbance units. As expected the progress of the reaction was indicated by a decrease of the absorbance due to 9,10-anthracene-dipropionic acid as shown in Fig. 7. Similarly a solution of rose bengal in the presence of ADPA was irradiated under identical conditions. From the ratio of rate constants, the apparent quantum yield of singlet oxygen geneation by the triangulenium ions (**1a**) was estimated as 0.36.

Singlet oxygen quantum yield in acetonitrile

Singlet oxygen production in acetonitrile was evaluated by using the absorbance of 1,3-diphenylisobenzofuran (DPBF). DPBF is a widely utilized singlet oxygen trapping-agent in organic solvents, which strongly absorbs light around 410–420 nm and emits bluish fluorescence. DPBF quantitatively reacts with $^1O_2$ through [4+2] cycloaddition to form an unstable endoperoxide and it forms *o*-dibenzoylbenzene at RT, which does not absorb visible light[40-42] (Scheme 3).

DPBF is a good acceptor and it reacts rapidly with $^1O_2$. It reacts neither with the ground state (triplet) molecular oxygen nor with the superoxide anion. Moreover its only reaction with $^1O_2$ is a chemical one[41]. Among the various singlet oxygen trapping agents DPBF has the largest rate constant for quenching singlet oxygen[43]. All the measurements were performed at RT in air-saturated solutions. To obtain singlet oxygen quantum yield we use the relative method, employed rose bengal in acetonitrile as standard and DPBF as the singlet oxygen probe (Fig. 8). This condition usually results in first-order kinetics.

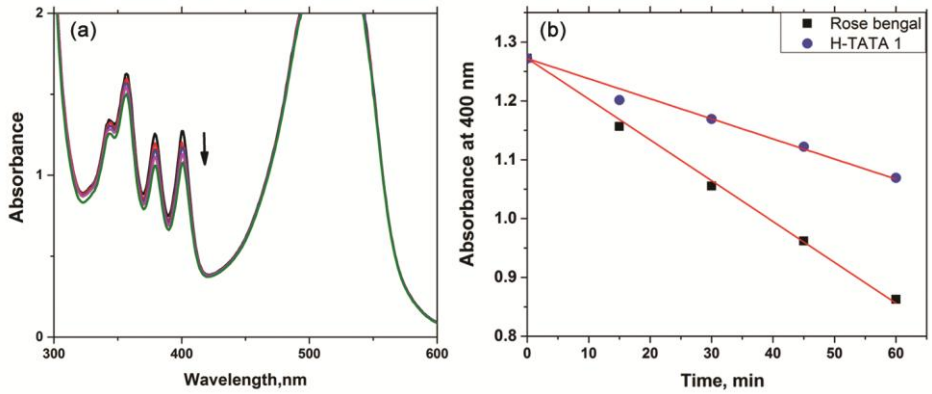


Fig. 7 — (a) Change in absorbance monitored at 400 nm of a solution of ADPA (1.8×10^{-4}M) and TATA (**1a**) (1.6×10^{-4}M) in saline buffer of *p*H=7 when irradiated at 530 nm (b) Comparison of the decrease in the absorbance at 400 nm of ADPA in presence of compound **1a** (●) in the presence of rose bengal (■)

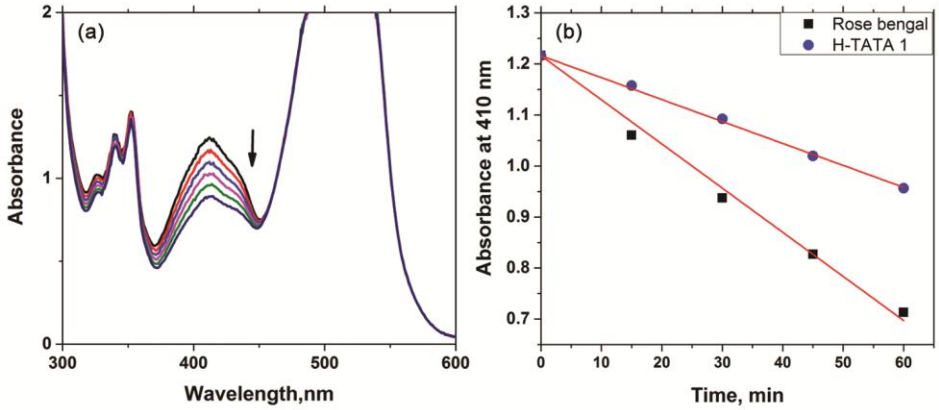
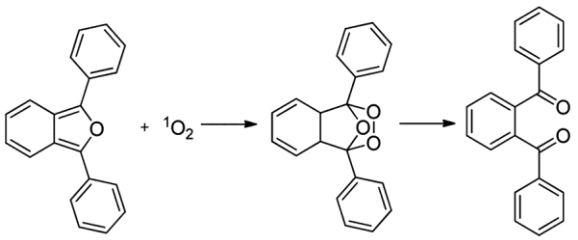


Fig. 8 — (a) Change in absorbance during the irradiation at 530 nm of a solution of DPBF (5.3×10^{-5} M) and **1a** (1.5×10^{-4} M) in acetonitrile. (b) Comparison of the decrease in the absorbance at 410 nm of DPBF(●) in the presence of rose bengal(■) and **1a** in acetonitrile.



Scheme 3

A blank irradiation in the absence of the **1a** was also carried out which did not show any change in the concentration of the DPBF. An air saturated solution of **1a** (1.5×10^{-4} M) in acetonitrile containing DPBF (5.3×10^{-5} M) was irradiated using 530 nm light. The photooxidation of DPBF was monitored spectrophotometrically. During the irradiation, no change in the absorbance of the dye solutions was observed indicating the absence of photobleaching under our experimental conditions. Under identical condition, the reference rose bengal (8.3×10^{-5} M) also irradiated in the presence of DPBF. For total absorption of the incident light the absorbance at the irradiation wavelength was ensured to be above 2 absorbance units. From the ratio of rate constants the apparent quantum yield of singlet oxygen geneation by the triangulenium ions **1a** was estimated as 0.21.

The role of singlet oxygen in TATA (1a) sensitized photooxidation

The competition kietics between ADPA and a singlet oxygen quencher N_3^- (NaN_3) was carried out to establish the role of $^1O_2$ in dye sensitized photooxidation. The presence of azide ion quenches the $^1O_2$, such an experiment reveal whether the dye sensitized photooxidation proceeds through $^1O_2$ mechanism or through a free radical intermediate. Fig. 9 shows the results of the competition between ADPA and N_3^- as $^1O_2$ quenchers in the presence of **1a**

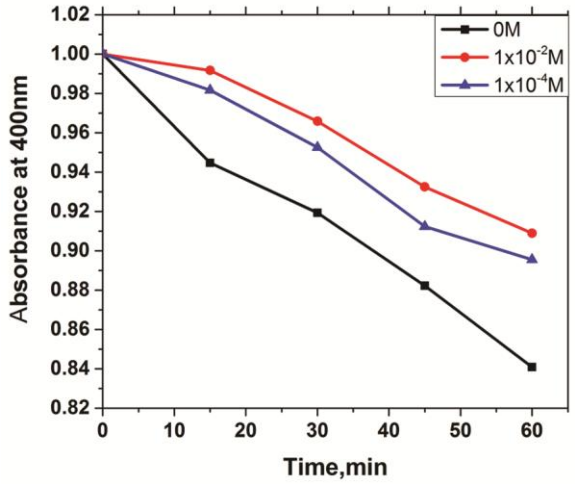


Fig. 9 — Competition for singlet oxygen between ADPA and N_3^- in the presence of **1a** with various quencher concentrations

as the sensitizer. The rate of singlet oxygen consumption has steadily decreased as a function of the azide anion concentration establishing the role of singlet oxygen in the photooxygenation of ADPA.

Conclusions

We have described the synthesis, photophysical properties and singlet oxygen generation efficiencies of a series of triazatriangulenium salts. The properties of these compounds in water and acetonitrile were compared. Both singlet and triplet lifetime of the compounds are higher in aqueous medium. Using absorption, fluorescence and phosphorescence spectra, the energy levels of the singlet and triplet excited states of the triazatriangulenium salts are determined. The singlet oxygen generation capacities of the synthesized compounds were determined using ADPA and DPBF as the chemical actinometers and rose bengal as the reference. The singlet oxygen quantum yield was found to be higher in aqueous medium than in acetonitrile.

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