CHAPTER 5
PHOTOPHYSICAL AND ELECTRON TRANSFER PROPERTIES OF A TRIAZATRIANGULENIUM CATION

5.1. Abstract

In this chapter we report the photophysical and electron transfer studies of the triazatriangulenium cation, \(4d^{\Theta}BF_4^\Theta\). Photophysical studies include absorption spectrum, fluorescence spectrum, fluorescence quantum yield, fluorescence lifetime and phosphorescence spectrum. The singlet and triplet energy levels of \(4d^{\Theta}BF_4^\Theta\) were obtained from these studies. The triplet state of the molecule was characterized using laser flash photolysis. We have observed that several electron acceptor molecules quenched the fluorescence of \(4d^{\Theta}BF_4^\Theta\). Laser flash photolysis studies have revealed that fluorescence quenching is due to electron transfer from the excited states of \(4d^{\Theta}BF_4^\Theta\) to the acceptor molecules. The effect of micellization on the PET reactions of \(4d^{\Theta}BF_4^\Theta\) was probed by flash photolysis experiments. Our studies show that micellization significantly affects the back electron transfer rates in these systems.

5.2. Introduction

Triaryl carbenium ions, containing ortho or para methoxy or chloro substituents can undergo aromatic nucleophilic substitution reactions \(S_{NAr}\) with alkyl amines under appropriate conditions.\(^{1-3}\) This observation has opened up a synthetic route to azatriangulenium ions.\(^{4-6}\) In earlier chapters of this thesis,
syntheses of monoaza- and diazatriangulenium systems were described. The synthesis of triazatriangulenium system is described in this chapter.

Laursen and Krebs have shown that triazatriangulenium derivatives 4a-c can be prepared from $\text{1}^{\text{a}}\text{BF}_4^{\oplus}$ in a one-pot reaction.\textsuperscript{5,6} The temperature required for the reaction is relatively high. For example, the tri-$n$-octyl derivative $4\text{c}^{\text{a}}\text{BF}_4^{\oplus}$ was obtained by refluxing $\text{1}^{\text{a}}\text{BF}_4^{\oplus}$ in a mixture of NMP and $n$-octylamine for 24 h. The reaction temperature required for the formation of the triaza- derivative could not be attained with low boiling amines such as methylamine or $n$-propylamine. However, when the reaction mixtures were buffered with benzoic acid, allowing the reflux temperatures to be raised sufficiently, the formation of $4\text{a}^{\text{a}}\text{BF}_4^{\oplus}$ and $4\text{b}^{\text{a}}\text{BF}_4^{\oplus}$ could be achieved within 10 – 24 h.

Formation of $4^{\text{a}}\text{BF}_4^{\oplus}$ in this reaction proceeds through the steps shown in Scheme 5.1. Evidence for the consecutive substitution of nitrogen atoms was obtained upon monitoring the reaction by mass spectrometry. The $S_NAr$ reactivity of the system decreases as the reaction proceeds, making it necessary to use high temperatures to affect complete transformation to $4^{\text{a}}\text{BF}_4^{\oplus}$. The decrease in reactivity at each stage can be explained by considering the redistribution of the positive charge, following each bridge formation. Upon bridge formation, the methoxy groups are replaced by strongly electron donating NR groups and this reduces the electrophilicity of the molecule. In fact, the reduction in reactivity of the monoaza- and diaza- derivatives towards $S_NAr$ reactions can be exploited to
synthesize asymmetric triaza-derivatives. Thus, the n-propylacridinium salt $2b^{\Theta}PF_6^{\Theta}$, upon refluxing with large excess of n-octylamine for 24 h, gave the unsymmetrical derivative $4e^{\Theta}PF_6^{\Theta}$. It is concluded that formation of the nitrogen-bridge is irreversible and that the SNAr approach is indeed suitable for the synthesis of more complex unsymmetrical triazatriangulenium systems.

Scheme 5.1
The triaza-derivative $4c^{\ominus}BF_4^{\ominus}$ can also be prepared by heating trioxatriangulenium tetrafluoroborate ($5^{\ominus}BF_4^{\ominus}$) with $n$-octylamine.\textsuperscript{6} In this case also the reaction proceeds in a stepwise manner as shown in Scheme 5.2.

![Scheme 5.2](image)

The reaction sequences described by Schemes 5.1 and 5.2 deal with inter- and intramolecular substitution in the ortho-methoxy-substituted triaryl carbenium ions. The key factors in these reactions are the reaction temperature, the nucleophilicity and the concentration of the amine.
X-ray crystallographic studies of some of the triazatriangulenium salts were carried out. These studies have shown that the triazatriangulenium skeleton is perfectly planar and disk like. When the alkyl groups are longer than \( n \)-propyl, these molecules form staggered dimers in the solid state, due to extensive \( \pi-\pi \) interactions. The \( pK_R^+ \) value of 4a was measured by UV-Vis spectrophotometry in DMSO/water/\( \text{Me}_4\text{NOH} \) solvent system. These measurements gave \( pK_R^+ = 23.7 \), which places 4a among the most stable carbenium ions, comparable in stability with the bis- and tris-(dimethylamino)-substituted triazulenyl carbenium ions recently synthesized by Ito and coworkers.

The chemistry of triazatriangulenium salts has not been explored. In this chapter, we report the photophysical and electron transfer properties of one derivative, namely 4,8,12-tri-\( n \)-butyl-4,8,12-triazatriangulenium tetrafluoroborate (4d\( ^\Theta \text{BF}_4 \)). Our studies revealed that 4d\( ^\Theta \text{BF}_4 \), in the excited state, is not a good electron acceptor. On the contrary, it exhibited properties of an electron donor.

The results of these investigations are described in the following section.

5.3. Results and discussion

As indicated earlier, 4d\( ^\Theta \text{BF}_4 \) is an extremely stable molecule. It is freely soluble in solvents such as acetonitrile, methanol and dichloromethane. It is insoluble in non-polar solvents such as hexane, benzene and toluene and also in water. It can, however, be dissolved in aqueous micellar solutions.
5.3.1. Absorption spectrum

$4d^\Theta BF_4^\Theta$ showed several absorption bands in the 250-570 nm region (Figure 5.1). The absorption band around 280 nm is very intense and sharp. There are two relatively weak bands, one centered around 350 nm and the other centered around 530 nm.

![Absorption spectrum](image)

**Figure 5.1.** Absorption spectrum of $4d^\Theta BF_4^\Theta$ in acetonitrile.

In Figure 5.2 we have compared the absorption spectra of the trioxatriangulenium ($5^\Theta BF_4^\Theta$) and the triazatriangulenium ($4d^\Theta BF_4^\Theta$) cations in the 400-600 nm region. It can be noticed that a change in the bridging hetero atom from oxygen to nitrogen is accompanied by a red shift of the absorption maximum by 45 nm and a two-fold intensity enhancement. The red shift observed is at variance with the trend seen in the case of xanthelium and acridinium systems, in which changing the hetero atom from oxygen to nitrogen causes a blue shift of 30 nm.\(^8\)
Figure 5.2. A comparison of absorption spectra of $5^\Theta\text{BF}_4^\Theta$ (....) and $4d^\Theta\text{BF}_4^\Theta$ (—) in acetonitrile.

It is interesting to notice that the long wavelength absorption band of $4d^\Theta\text{BF}_4^\Theta$ is blue shifted compared to that of the azadioxa- and diazaoxa-derivatives described in earlier chapters of this thesis. It should also be pointed out that the absorption bands of the trioxa- and triazatriangulenium salts have little structure, in contrast to the structured absorption bands of the monoaza- and diaza-derivatives. This is also in line with the general observation that unsymmetrical triaryl carbenium ions exhibit broad, structured absorption bands in the visible region.
5.3.2. Fluorescence spectrum

4d$^@_{\text{BF}_4^\Theta}$ exhibited fluorescence in the 525-700 nm region. In Figure 5.3 the fluorescence spectrum of 4d$^@_{\text{BF}_4^\Theta}$ is shown along with that of 5$^\Theta_{\text{BF}_4^\Theta}$.

![Fluorescence spectrum graph](image)

**Figure 5.3.** Fluorescence spectra of 4d$^@_{\text{BF}_4^\Theta}$ (→) and 5$^\Theta_{\text{BF}_4^\Theta}$ (.....) in acetonitrile.

The fluorescence quantum yield ($\Phi_F$) of 4d$^@_{\text{BF}_4^\Theta}$ was determined in a few solvents by the relative method. Optically matched solution of Rhodamine-6G in ethanol was used as the standard and $\Phi_F$ was calculated as described in Chapter 2 of this thesis. Fluorescence decay of 4d$^@_{\text{BF}_4^\Theta}$ was monoexponential in all the solvents used. The fluorescence decay profile obtained in acetonitrile is shown in Figure 5.4.
Figure 5.4. (a) Fluorescence decay profile of $4d^{10}\text{BF}_4^-$ in acetonitrile. (b) is the lamp profile. Excitation and emission wavelengths were 486 and 557 nm, respectively.

The photophysical properties of $4d^{10}\text{BF}_4^-$ in three solvents are summarized in Table 5.1. From the point of intersection of the absorption and fluorescence spectra, the singlet energy of $4d^{10}\text{BF}_4^-$ was calculated and the value obtained was 51.2 kcal M$^{-1}$. 
Table 5.1. Absorption maxima ($\lambda_{\text{max}} \text{(abs)}$), extinction coefficients ($\varepsilon_{\text{max}}$), emission max ($\lambda_{\text{max}} \text{(em)}$), singlet lifetime ($\tau_F$) and singlet quantum yield ($\Phi_F$) of $4d^{6}\text{BF}_4^{\text{-}}$ in acetonitrile, dichloromethane and methanol.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}} \text{(abs)}$ nm</th>
<th>$\varepsilon_{\text{max}}$, M$^{-1}$ cm$^{-1}$</th>
<th>$\lambda_{\text{max}} \text{(em)}$ nm</th>
<th>$\tau_F$, ns</th>
<th>$\Phi_F$</th>
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<td>333</td>
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<tr>
<td></td>
<td>352</td>
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<td>557</td>
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<td>525</td>
<td>$6.75 \times 10^4$</td>
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<td>525</td>
<td>$6.75 \times 10^4$</td>
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5.3.3. Phosphorescence spectrum

The low $\Phi_F$ value for $4d^{6}\text{BF}_4^-$ suggests alternate modes of deactivation for its singlet excited state. This has prompted us to look for phosphorescence emission from $4d^{6}\text{BF}_4^-$. We observed that $4d^{6}\text{BF}_4^-$ exhibits very good phosphorescence at 77 K in methanol glass. The phosphorescence spectrum we obtained under this condition is shown in Figure 5.5.

![Phosphorescence spectrum of 4d6BF4- in methanol glass at 77K. Excitation wavelength was 486 nm.](image)

**Figure 5.5.** Phosphorescence spectrum of $4d^{6}\text{BF}_4^-$ in methanol glass at 77K. Excitation wavelength was 486 nm.

Since the phosphorescence spectrum did not show any structure, the onset of the emission in Figure 5.5 was taken as the 0-0 band position and using this wavelength the triplet energy of $4d^{6}\text{BF}_4^-$ was calculated. This calculation gave a value of 48.2 kcal M$^{-1}$ for the triplet energy of $4d^{6}\text{BF}_4^-$. The photophysical
studies thus enabled us to determine the energy levels of the various excited states of $4d^{\@}BF_4^\@$. A schematic diagram is shown below.

![Schematic diagram](image)

Figure 5.6. Schematic representation of the energy levels in $4d^{\@}BF_4^\@$.

Figure 5.6 shows that the S-T energy gap for $4d^{\@}BF_4^\@$ is only 3 kcal M$^{-1}$. This value is much smaller than those observed for pyrylium salts$^{10}$ and even smaller than those observed for several aromatic ketones.$^{11}$ The S-T energy gap obtained in this case is similar to that observed in the case of the trioxatriangulene derivative $5^{\@}BF_4^\@$. The small S-T energy gap facilitates intersystem crossing and lead to high triplet quantum yield for $4d^{\@}BF_4^\@$.

5.3.4. Laser flash photolysis studies

In order to gain a detailed understanding of the excited state properties of $4d^{\@}BF_4^\@$, laser flash photolysis experiments were carried out. Excitation of $4d^{\@}BF_4^\@$ using the 532 nm light from a Nd:YAG laser resulted in the transient absorption spectrum shown in Figure 5.7.
Figure 5.7. Transient absorption spectrum of $4d^{9}\text{BF}_4^-$ (2 x $10^{-4}$ M) in acetonitrile at 1.4 µs after laser excitation at 532 nm.

The transient spectrum exhibited absorption maxima at 310, 420 and 660 nm and bleaching in the 400-530 nm region. The bleaching in the 400-530 nm region is attributed to the ground state absorption of $4d^{9}\text{BF}_4^-$. The transient decayed with a lifetime of 5 µs and the decay kinetics were the same at all wavelengths. The decay at 420 nm and bleach recovery at 520 nm are shown in Figure 5.8.

Figure 5.8. Kinetic profiles of $4d^{9}\text{BF}_4^-$ at (a) 420 nm and (b) 520 nm.
The triplet quantum yield of \(4d^\oplus BF_4^\ominus\) was determined using the energy transfer method (see Chapter 3, for details). We have obtained 0.68 as the triplet quantum yield of \(4d^\oplus BF_4^\ominus\). Thus \(\Phi_F + \Phi_T = 0.93\) for \(4d^\oplus BF_4^\ominus\) in dichloromethane solution, which suggests that no other significant deactivation pathways are available for \(4d^\oplus BF_4^\ominus\) in this solvent.

5.3.5. Electrochemical studies

Voltammetric measurements were carried out in order to determine the redox potentials of \(4d^\oplus BF_4^\ominus\). Cyclic voltammograms obtained showed the presence of irreversible reduction and oxidation peaks for \(4d^\oplus BF_4^\ominus\). In order to get the accurate redox potentials, the SWV voltammograms were obtained in acetonitrile solution. Figure 5.9 gives the SWV voltammogram of \(4d^\oplus BF_4^\ominus\) in acetonitrile. The voltammogram exhibited an oxidation peak at 1.2 V and a reduction peak at -1.4 V (both vs. SCE). The oxidation potential of \(4d^\oplus BF_4^\ominus\) is comparable to those of aromatic hydrocarbon donors such as anthracene or pyrene and its reduction potential is comparable to those of aromatic acceptors such as \(p\)-dicyanobenzene or \(p\)-cyanobenzoate. This suggests that \(4d^\oplus BF_4^\ominus\) may act as an acceptor or donor, depending on the conditions available.
Figure 5.9. Square wave voltammogram of 4d\(^\Theta\)BF\(_4\Theta\). (a) reduction side and (b) oxidation side.

5.3.6. Electron transfer studies

5.3.6.1. Fluorescence quenching studies

In earlier chapters of this thesis, we have observed that good electron donors such as arylamines and phenothiazines quenched the fluorescence of the trioxa-, azadioxa- and diazaoxatriangulenium salts very efficiently. These electron donors, however, had no influence on the fluorescence of the triaza- derivative 4d\(^\Theta\)BF\(_4\Theta\). These experiments have revealed that the singlet excited state of 4d\(^\Theta\)BF\(_4\Theta\) is not a good electron acceptor. Using the Weller equation\(^{12}\), we have calculated the \(\Delta G^0\) values for electron transfer from arylamines and phenothiazines to the singlet excited state of 4d\(^\Theta\)BF\(_4\Theta\). The \(\Delta G^0\) values obtained were positive for all aryl amines and -0.07 for phenothiazine derivatives,
indicating that these electron transfer processes are thermodynamically not favoured.

The fluorescence of $4d^{\Theta}BF_4^{\Theta}$, however, was quenched efficiently by several electron acceptors. The quenchers we have employed include several quinones, nitroaromatics and methyl viologen. All these molecules have their absorption maximum at shorter wavelengths compared to $4d^{\Theta}BF_4^{\Theta}$. This ruled out any quenching due to energy transfer. Quenching due to exciplex formation can also be ruled out because we did not observe any emission bands that can be assigned to exciplexes in these experiments. Hence the fluorescence quenching in these cases must be due to electron transfer processes.

Figure 5.10 shows the fluorescence spectra of $4d^{\Theta}BF_4^{\Theta}$ in acetonitrile in the presence of various concentrations of DDQ. Similar fluorescence quenching patterns were obtained in the case of other quenchers employed.
Figure 5.10. Fluorescence spectra of $4d^{\Theta}BF_4^\Theta$ ($2 \times 10^{-5}$ M) in the presence of DDQ. [DDQ] were: (a) 0 mM, (b) 1 mM (c) 2 mM, (d) 3 mM and (e) 4 mM.

In all the cases studied, plots of fluorescence intensity vs. quencher concentration [Q], were linear and followed the Stern-Völmer equation (see Chapter 2 for details). Representative examples of the Stern-Völmer plots obtained in the fluorescence quenching of $4d^{\Theta}BF_4^\Theta$ are given in Figure 5.11.

Figure 5.11. Stern-Völmer plots for the fluorescence quenching of $4d^{\Theta}BF_4^\Theta$. The quenchers were: (O) Chloranil, (Δ) $p$-benzoquinone and (□) $m$-dinitrobenzene.
Stern-Volmer constants \((K_{SV})\) obtained for the various quenchers were in the range of 0.5 \(M^{-1}\) to 238 \(M^{-1}\) (Table 5.2). From the \(K_{SV}\) values and known \(\tau_F\) values, the \(k_q^S\) values were calculated and these are presented in Table 5.2. Notice that \(k_q^S\) values varied in a wide range of \(6.1 \times 10^7\) to \(2.55 \times 10^{10} \ M^{-1} \ s^{-1}\).

Table 5.2. List of quenchers, their reduction potentials \((E_{\text{red}} \text{ vs. SCE})\), \(\Delta G^0\) values, Stern-Volmer quenching constants \((K_{SV})\) and fluorescence quenching rate constants \((k_q^S)\) for the electron transfer quenching of 4d\(^{6}\)BF\(_4\)\(^{-}\).

<table>
<thead>
<tr>
<th>Quenchers</th>
<th>(E_{\text{red}}, V^a)</th>
<th>(\Delta G^0, eV)</th>
<th>(K_{SV}, M^{-1})</th>
<th>(k_q^S, 10^9 M^{-1} s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(o)-Nitrotoluene</td>
<td>-1.26</td>
<td>0.21</td>
<td>0.51</td>
<td>0.06</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>-1.15</td>
<td>0.12</td>
<td>7.05</td>
<td>0.75</td>
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<tr>
<td>(m)-dinitrobenzene</td>
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<td>-0.15</td>
<td>67.00</td>
<td>7.14</td>
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<tr>
<td>(p)-benzoquinone</td>
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<td>-0.51</td>
<td>180.00</td>
<td>12.11</td>
</tr>
<tr>
<td>Methylviologen</td>
<td>-0.47</td>
<td>-0.62</td>
<td>116.00</td>
<td>12.30</td>
</tr>
<tr>
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<td>-1.05</td>
<td>148.00</td>
<td>15.55</td>
</tr>
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<td>DDQ</td>
<td>0.51</td>
<td>-1.59</td>
<td>238.00</td>
<td>25.29</td>
</tr>
</tbody>
</table>

\(^a\) taken from references 13-15.
5.3.6.2. Correlation of fluorescence quenching constants with $\Delta G^\circ$

As mentioned earlier, fluorescence quenchings in these cases occur most probably due to electron transfer mechanism. All the quenchers used are good electron acceptors (see Table 5.2 for the reduction potentials of the quenchers). Hence the mechanism in these cases most probably involve a transfer of an electron from the singlet excited state of $4d^\oplus_{BF_4}^\Theta$ to the acceptor molecule as shown in Equation 5.1.

$$*4d^\oplus + A \xrightarrow{ET} 4d^{2+} + A^-$$  \hspace{1cm} (5.1)

In order to correlate the fluorescence quenching rate constants to the free energy changes ($\Delta G^\circ$) associated with these reactions, we have calculated the $\Delta G^\circ$ values using the Weller equation.\(^\text{12}\) Since the electron transfer described by equation 5.1 proceeds with a change in the number of charges, the coulombic term in the Weller equation has a non-zero value. For the present case, the coulombic term was calculated assuming a value of 7 Å for the center-to-center distance. For this calculation, we neglected the alkyl groups because these are not participating in the electron transfer processes. $\Delta G^\circ$ values thus calculated are also presented in Table 5.2. Notice that $\Delta G^\circ$ varied in the range of $+0.21$ eV to $-1.05$ eV for the different quenchers.
In order to ascertain the electron transfer mechanism of quenching, we have attempted to correlate the observed quenching rate constants with the calculated $\Delta G^0$ values (see Chapter 2 for details). In Figure 5.12, the experimental $k_q^S$ values are presented along with a Rehm-Weller fit.\textsuperscript{12} For the fit shown in Figure 5.12, values of $\Delta G^0 = 0.07 \text{ eV}$ and $k_{\text{dis}} = 3.7 \times 10^{10} \text{ M}^{-1} \text{s}^{-1}$ were used. It can be seen from Figure 5.12 that the fit is very good and this confirms the electron transfer pathway for the quenching of the fluorescence of $4d^8\text{BF}_4^\Theta$ by electron acceptors. As described in the case of the diazaoxatriangulenium derivative, quenching in this case also may proceed through the various stages shown in Figure 4.12 (see Chapter 4).

![Figure 5.12. Plot of log $k_q^S$ vs. $\Delta G^0$. Solid line is a fit to the Rehm-Weller equation.](image-url)
5.3.6.3. Laser flash photolysis studies

In order to gain a better understanding of the electron transfer processes involved in the fluorescence quenching of $4d^{\oplus}\text{BF}_4^\ominus$, laser flash photolysis experiments were carried out. Figure 5.13 is the transient absorption spectrum obtained upon irradiation of a solution of $4d^{\oplus}\text{BF}_4^\ominus$ (2 x $10^{-4}$ M) in the presence of $p$-benzoquinone (0.01 M).

![Graph showing transient absorption spectrum](image)

**Figure 5.13.** Transient absorption spectrum of obtained at 1.5 µs following the excitation of $4d^{\oplus}\text{BF}_4^\ominus$ (2 x $10^{-4}$ M) in acetonitrile in the presence of $p$-benzoquinone (0.01 M).

According to Equation 5.1, electron transfer leads to the formation of benzoquinone radical anion ($\text{BzP}^-$) and $4d^{++++}$. The absorption spectrum of $\text{BzP}^-$ exhibited bands at 325, 428 and 458 nm.\textsuperscript{16,17} Thus in Figure 5.13, bands at 320, 420 and 450 nm can be attributed to $\text{BzP}^-$. The remaining bands (360, 510, 580
and 670 nm) can be attributed to $4d^{++}$. The decay profiles at 450 nm is shown in Figure 5.14.

![Graph showing kinetic decays observed at 450 and in the flash photolysis of the 4d\(^{\Theta}\)BF\(_4\)\(^{\Theta}\)/BzP system.](image)

**Figure 5.14.** Kinetic decays observed at 450 and in the flash photolysis of the 4d\(^{\Theta}\)BF\(_4\)\(^{\Theta}\)/BzP system.

We have assigned the absorption bands at 360, 510, 580 and 680 nm in the above experiment to $4d^{++}$. In order to confirm this assignment, flash photolysis of $4d^{\Theta}\)BF\(_4\)\(^{\Theta}\) was carried out in the presence of another well-known electron acceptor, methyl viologen (MV\(^{2+}\)). Electron transfer from $4d^{\Theta}\)BF\(_4\)\(^{\Theta}\) to MV\(^{2+}\) should generate $4d^{+++}$ and MV\(^{++}\) according to equation 5.1. The transient absorption spectrum obtained in this case is given in Figure 5.15.
Figure 5.15. Transient absorption spectrum at 1.5 μs after laser excitation, for the 4d\(^{6}\)BF\(_{4}\)^{-}/MV\(^{2+}\) system.

The absorption bands at 390 and 610 nm\(^{18,19}\) are due to the well-known MV\(^{++}\). The remaining absorption bands can be attributed to 4d\(^{++}\). The absorptions due to MV\(^{++}\) are very strong and mask other absorption bands. Even then, we can notice that all the absorption bands (360, 510, 580 and 670 nm) attributed to 4d\(^{++}\) are present (mostly as shoulders to other strong absorptions) in Figure 5.15. We conclude that these absorptions can undoubtedly be assigned to 4d\(^{++}\).

5.3.7. Triplet quenching experiments

We have observed that the triplet absorption due to 4d\(^{6}\)BF\(_{4}\)^{-} at 660 nm is quenched very efficiently by anthracene (An). Quenching of the triplet is accompanied by the growth of a transient absorption at 420 nm. Figure 5.16 shows the decay at 660 nm and growth at 420 nm, in the flash photolysis of 4d\(^{6}\)BF\(_{4}\)^{-}, as a function of An concentration.
Figure 5.16. Decay at 660 nm and growth at 420 nm in the flash photolysis of 4d$^\oplus$BF$_4^\ominus$/An system. [An] were: (a) 1 x 10$^{-5}$, (b) 2 x 10$^{-5}$, (c) 3 x 10$^{-5}$ and (d) 4 x 10$^{-5}$ M.

Plot of the pseudo-first-order rate constants ($k_{obs}$) against [An] was linear (Figure 5.17) and from this graph the triplet quenching rate constant ($k_q^T$) was calculated as described in Chapter 2 of this thesis. We obtained a value of 8.3 x 10$^9$ M$^{-1}$ s$^{-1}$ for $k_q^T$ in this case.

![Graph](image1.png)

Figure 5.17. Plot of $k_{obs}$ vs. [An] for the 4d$^\oplus$BF$_4^\ominus$/An system. The monitoring wavelength was 660 nm.
For An, the oxidation potential is +1.09 V and reduction potential is −1.95 V (both vs. SCE). These values suggest that electron transfers involving the excited states of 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖} and ground state of An (ET from *4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖} to An or ET from An to *4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖}) are thermodynamically unfavourable. Thus, excitation of 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖} in the presence of An is not expected to generate radical ion products. It is to be noticed, however, that the triplet energy of 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖} (48.2 kcal M\textsuperscript{−1}) is higher than that of An (42.5 kcal M\textsuperscript{−1}). Thus, excitation of 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖} in the presence of An should result in triplet-triplet energy transfer. In order to confirm the T-T energy transfer process, we have recorded the transient absorption spectra of the 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖}/An system at different time intervals following the laser excitation and these are shown in Figure 5.18.

![Figure 5.18](image)

**Figure 5.18.** Transient absorption spectra for the 4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖}/An system at (Δ) 0.28, (O) 1.0 and (◊) 2.0 μs after the laser pulse. [4d\textsuperscript{⊕}BF\textsubscript{4}\textsuperscript{⊖}] was 2 x 10\textsuperscript{−4} M and [An] was 4 x 10\textsuperscript{−5} M.
It can be seen from Figure 5.18 that the transient absorption assigned to the triplet of $4d^{6}\text{BF}_4^-$ decays with concomitant formation of absorption at 420 nm. The transient spectrum that finally emerges is the T-T absorption spectrum of An. We conclude that quenching of the triplet of $4d^{6}\text{BF}_4^-$ by An results in triplet-triplet energy transfer.

5.3.8. PET reactions of $4d^{6}\text{BF}_4^-$ in SDS micelles

As mentioned in Chapter 1 of this thesis, a major objective of research in photoinduced electron transfer is to devise methods to reduce the rate of BET reactions. Micelles have proven to be very valuable in the attempts to reduce BET rates. A micelle is a spherical aggregate formed when surfactant molecules are dissolved in aqueous media, at concentrations above their critical micelle concentration. Micelles have a hydrocarbon like core and a polar or charged outer surface. The hydrocarbon core can dissolve organic molecules. The ionic head groups attract those molecules having opposite charge and repel those having the same charge. Thus, the micelles can be used to partition ionic reaction products. This property of the micelles has been utilized in obtaining long-lived radical products in PET reactions and several reviews dealing with this subject are currently available in the literature.

For all the triangulene derivatives studied in this thesis, we have attempted to carry out PET reactions in micellar solutions. The trioxa-, azadioxa- and diazaoxatriangulenium salts, described in earlier chapters of this thesis, could not
be properly micellized. The triazatriangulenium derivative \(4d^\Theta BF_4^\Theta\) could be dissolved in micelles in sufficient concentrations. In all probability, micellization in this case can be attributed to the presence of the three alkyl chains present in the molecule. In this section, we briefly describe the photophysical and electron transfer properties of \(4d^\Theta BF_4^\Theta\) in micellar solutions of sodium dodecyl sulfate (SDS).

Micellization of \(4d^\Theta BF_4^\Theta\) leads to slight changes in its absorption and emission properties. The absorption and fluorescence spectra of \(4d^\Theta BF_4^\Theta\) in acetonitrile and SDS solutions are compared in Figures 5.19 and 5.20.

![Figure 5.19. Absorption spectra of \(4d^\Theta BF_4^\Theta\) in acetonitrile (—) and SDS solutions (....).](image)
Figure 5. 20. Fluorescence spectra of $4d^8\text{BF}_4^-$ in acetonitrile (—) and SDS solutions (....).

Changes in the absorption and fluorescence maxima can be taken as evidence for the micellization of $4d^8\text{BF}_4^-$. The fluorescence lifetime of $4d^8\text{BF}_4^-$ increases to 11.1 ns in SDS micelles. The absorption and fluorescence measurements, however, have not provided any information regarding the solubilization site of $4d^8\text{BF}_4^-$ within the micelle. Since $4d^8$ is positively charged and insoluble in hydrocarbon solvents, its most probable location in the micelle would be the polar outer region. Most probably, the molecule will have its rigid core sitting near the head groups with the hydrocarbon chains buried within the hydrocarbon core. The $\text{BF}_4^-$ counter ion, most probably, will be loosely bound in the Stern layer of the micelle.
5.3.8.1. Laser flash photolysis studies

In order to study the effect of micellization on the PET reactions of $4d^{\oplus}BF_4^\ominus$, flash photolysis experiments were carried out. Transient absorption spectra obtained for the $4d^{\oplus}BF_4^\ominus/Bzp$ and $4d^{\oplus}BF_4^\ominus/MV^{2+}$ systems indicated that PET reactions take place in micellar solutions also. Absorptions corresponding to the radical products were obtained in both cases. The decay profiles obtained, however, were very different (compared to those in homogeneous solutions) and indicated that the back electron transfer pathways are significantly modified in the presence of micelles.

The decay profiles of the $Bzp^-$ absorptions at 420 nm, obtained in the flash photolysis of $4d^{\oplus}BF_4^\ominus/Bzp$ system in acetonitrile and SDS solutions are compared in Figure 5.21. In acetonitrile solution complete decay of $Bzp^-$ occurs within 20 µs, whereas in SDS micelles the decay was not complete even after 5 milliseconds. Thus, the BET rate is 1000 times slower for this system in SDS micelles.
Figure 5.21. Decay of BzP\(^*\) monitored at 420 nm in the flash photolysis of 4d\(^{\Theta}\)BF\(\Theta^4\)/BzP system. (a) in acetonitrile and (b) in SDS micelles.

For the 4d\(^{\Theta}\)BF\(\Theta^4\)/BzP system, electron transfer leads to the formation of 4d\(^{++}\) and BzP\(^*\) as mentioned earlier (see equation 5.1 also). SDS being anionic micelle, attracts and holds the 4d\(^{++}\) species. The BzP\(^*\) species, on the other hand, is negatively charged and will be expelled from the micelle. The products of electron transfer are separated by these coulombic interactions. The back electron transfer is considerably reduced leading to extremely long lived radical species.

The decay profiles of the MV\(^{++}\) absorptions at 610 nm, obtained in the flash photolysis of 4d\(^{\Theta}\)BF\(\Theta^4\)/MV\(^{2+}\) system in methanol and SDS solutions, are compared in Figure 5.22. In methanol solution, the MV\(^{++}\) species is slowly formed and the decay of this species takes several microseconds to complete (Figure 5.22 a). In SDS micelles, on the other hand, the MV\(^{++}\) species decays extremely rapidly (Figure 5.22 b). This shows that the BET rate is enhanced several fold in this case.
Electron transfer in $4d^{6}\text{BF}_4^{-}/\text{MV}^{2+}$ system leads to the formation of $4d^{++}$ and $\text{MV}^{++}$ as mentioned earlier (see equation 5.1 also). SDS being anionic micelle, attract and hold both these cationic entities. The products are thus confined within the small volume near the head group region of the micelle resulting in a rapid BET reaction. These studies show that the micellar environment can modify the kinetics of electron transfer reactions in a significant manner.

5.3.9. Comparative study of the triangulenium cations

The carbenium ions, namely trioxatriangulenium, azadoxatriangulenium, diazaoxatriangulenium and triazatriangulenium cations, present an interesting case for a comparative study. In this thesis, we have looked into the photophysical and electron transfer properties of these cations and only these aspects will be considered here.
The trioxa- and triazatriangulenium cations are highly symmetrical. These cations have their absorption and fluorescence spectra blue shifted in comparison to the less symmetrical azadioxa- and diazaoxatriangulenium derivatives. The symmetrical cations have comparatively lower fluorescence quantum yields and fluorescence lifetimes. They also exhibited high triplet quantum yields and good phosphorescence emissions. For these two cations, $\Phi_F + \Phi_T \approx 1$, which indicated that other non-radiative pathways are not involved in the deactivation of their singlet excited states. The unsymmetrical azadioxa- and diazaoxa- derivatives did not exhibit phosphorescence and their triplet quantum yields were also very low. In these cases, $\Phi_F + \Phi_T < 1$, meaning that other non-radiative pathways are involved in the deactivation of their singlet excited states.

The redox potentials of these cations exhibit a progressive shift with increasing number of skeletal nitrogen atoms. The trioxa- derivative has a very low oxidation potential. Replacing the oxygen atoms by NR ($R = \text{alkyl}$) groups significantly reduces the oxidizing power of the molecule. As we increase the number of NR groups, the reduction potential becomes increasingly negative. The oxidation potential exhibits the opposite trend. The trioxa- and azadioxa-derivatives did not exhibit any oxidation peaks. The diazaoxa- and triaza-derivatives exhibit oxidation peaks around 1.2 V vs. SCE. Thus, increasing the number of nitrogen atoms has the effect of converting the molecule from an electron acceptor to an electron donor.
Fluorescence quenching and laser flash photolysis studies have corroborated the above observations. The trioxa- derivative is a very good electron acceptor in its singlet and triplet excited states. It can accept electrons even from hydrocarbons such as benzene or toluene. The azadioxa- derivative is also a good electron acceptor in the singlet excited state, although its oxidizing power is much lower compared to the trioxa- derivative. The diazaoxa- derivative is a poor electron acceptor in its singlet state as it could accept electrons only from the strongest of electron donors. This molecule also exhibited properties of a poor electron donor. The triaza- derivative is not an excited state electron acceptor. The molecule, on the other hand, exhibited moderate electron donating abilities. Thus, upon going from the azadioxa- to the triaza- derivative, we see a gradual shift of PET property, from an excited state acceptor to an excited state donor. As mentioned earlier in this thesis, carbenium ions are generally good electron acceptors. Carbenium ions exhibiting electron donating properties are very rare and the diazaoxa- and triazatriangulenium cations belong to this small group of carbenium ions.

5.4. Summary and conclusions

In this chapter we have studied the photophysical and electron transfer properties of triazatriangulenium tetrafluoroborate (4d\(^{\text{BF}_4}\)). Using absorption, fluorescence and phosphorescence spectra, the energy levels of the singlet and triplet excited states of 4d\(^{\text{BF}_4}\) were determined. The fluorescence of 4d\(^{\text{BF}_4}\)
was quenched by several electron acceptors and our studies have established that
the quenching proceeds through an electron transfer mechanism. The quenching
rate constants were analyzed using the Rehm-Weller equation. The electron
transfer mechanism was further confirmed by laser flash photolysis studies.
$4d^{\theta}BF_4^\Theta$ could be dissolved in SDS micelles. The effect of micellization on the
PET reactions of $4d^{\theta}BF_4^\Theta$ was probed by flash photolysis experiments. Our
studies show that micellization significantly affects the back electron transfer rates
in these systems.

5.5. Experimental

Triazatriangulenium tetrafluoroborate ($4d^{\theta}BF_4^\Theta$) was synthesized by the
adaptation of a reported procedure.\textsuperscript{5} The following spectrosocopic data are obtained for
the compound $4b^{\theta}BF_4^\Theta$: Yield 30%; mp > 300°C; IR ($\nu_{\text{max}}$): 3494, 2955, 2369,
1613, 1572, 1243, 1040 cm$^{-1}$; $^1$HNMR (300 MHz, CD$_3$CN): $\delta$ 7.907-7.962 (t, 3H), 7.091-7.229 (d, 2H), 4.067-4.117 (t, 6H), 1.039-2.205 (m, 21H);
$^{13}$CNMR (75 MHz, CD$_3$CN): $\delta$ 141.208, 140.960, 138.692, 118.446, 106.098,
48.598, 27.540, 30.629, 14.213; Anal. Calcd: C, 69.27; H, 6.75; N, 7.81. Found:
C, 68.94; H, 7.43; N, 7.13.

$m$-Dinitrobenzene was prepared by the nitration of nitrobenzene.\textsuperscript{32} Other
quenchers were commercial samples and were purified by recrystallization or
distillation. Solvents used were of spectroscopic grade. Doubly distilled water was
used. SDS was a commercial sample from Aldrich. Micellar solutions were prepared by injecting a small volume of a concentrated solution (in acetonitrile) of $4d@\text{BF}_4^-$ into a solution of SDS (25 mM) in water. The solution was sonicated for 1h and kept aside for overnight. It was then filtered and the clear solution obtained was used for the photophysical studies.

Absorption spectra were recorded on a Shimadzu-3101 PC UV-Vis NIR Scanning spectrophotometer. Fluorescence spectra were recorded on a SPEX fluorolog F-112 X spectrofluorimeter. Phosphorescence spectrum was recorded on a SPEX 1934 D phosphorimeter. Fluorescence lifetimes were determined using an Edinburgh FL900CD Single Photon Counting System. Redox potentials were measured using a BAS CV50 W Cyclic Voltammetric Analyzer. A solution of $4d@\text{BF}_4^-$ (1 x 10^{-3} M) in acetonitrile containing 0.1 M tetra-n-butylammonium tetrafluoroborate as supporting electrolyte was thoroughly degassed before use. A glassy carbon electrode was used as the working electrode and a platinum gauze was used as the counter electrode. A silver wire was used as the reference electrode. The potential values were corrected by recording the oxidation potential of ferrocene under identical conditions. Laser flash photolysis experiments were carried out using an Applied Photophysics Model LKS-20 Laser Kinetic Spectrometer using a GCR-12 Series Quanta Ray Nd:YAG laser. The excitation wavelength was 532 nm.
5.6. References


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