Chapter 1

Long-lived Photoinduced Charge Separation in Molecular Systems: An Overview

1.1. Introduction

Energy is one of the most important issues of the twenty-first century. At present the energy needed is supplied mainly by the use of fossil fuels. Estimates indicate that the energy consumption will increase at least two-fold, from our current burn rate of 12.8 TW to 28-35 TW by the year 2050. World reserves of fossil fuels are progressively decreasing and the projected requirements would not be met by fossil fuel sources alone. In addition, continued use of fossil fuels leads to global warming and pollution problems that threatens human health and creates environmental issues. Therefore use of renewable and clean energy resources is definitely required in order to solve the global energy and environmental issues. Solar energy is one of the most important alternate energy sources that can be exploited to meet our future energy demands. Solar energy can be converted into useful energy forms such as heat, electricity or fuels. However, technologies leading to efficient use of solar energy have not yet been fully developed.
Solar energy can be harvested by direct or indirect pathways. Indirect pathways include processes such as conversion of biomass to biogas or production of hydrogen by electrolysis of water using electricity from photovoltaics. Direct pathways include photovoltaics and production of fuels such as hydrogen using integrated systems. Artificial photosynthesis is an example of direct sunlight utilization. The basis of artificial photosynthesis is not to copy the photosynthetic process in the laboratory but to learn from the natural photosynthetic process and use some of its essential principles to design systems capable of producing energy or fuels.

Light excitation can induce a variety of chemical reactions. For energy-conversion purposes, photoinduced electron transfer (PET) is by far the preferred reaction in nature. It is a thoroughly investigated process in natural and artificial systems. PET involves the transfer of an electron from a donor molecule (D) to an acceptor molecule (A) without making or breaking any chemical bonds. Prior to electron transfer one of the components is excited with light. Understanding the process of PET helps scientists to design potential systems for artificial photosynthesis, which ultimately aims in mimicking green plants and other photosynthetic organisms that are using sunlight to make high-energy chemicals. PET results in the formation of product ions (donor radical cation D$^{+*}$ and acceptor radical anion A$^{-*}$) which are at higher energy levels compared to the starting D and A molecules. The term ‘conversion of solar energy into chemical energy’ actually
means the generation of a high-energy charge separated (CS) state by way of light absorption. The CS state generated in PET reactions is generally short-lived and undergo 'back electron transfer' (BET) to generate the D-A system in their ground state, thereby leading to wastage of the absorbed energy as shown in Scheme 1.1.

**Scheme 1.1. Schematic of PET and BET in intermolecular D-A systems**

The D and A units can also be linked by covalent bonds or non-covalent interactions, as shown in Scheme 1.2. Upon excitation, intramolecular electron transfer takes place from D to A leading to the formation of a CS state. Possibility of fast energy wasting BET exists in these cases also.

**Scheme 1.2. Schematic of PET and BET in covalently linked D-A systems**
In Schemes 1.1 and 1.2, BET represents the energy wasting back electron transfer reaction. In simple donor-acceptor systems, $D^{*+}$ and $A^{-}$ are formed at close proximity which facilitates the BET reaction. BET reaction reduces the yield and lifetime of the CS state. This energy wasting step is a serious limitation of PET reactions in simple D-A systems. A large number of D-A systems have been studied in order to elucidate the charge separation and recombination mechanisms and also to assess the efficiency and practical applicability of such molecular systems. These studies have led to important advances in the theory and practice of electron-transfer reactions. Studies on the photophysical and photochemical processes involved in the natural photosynthetic reaction center also have guided the efforts in this direction.

The photosynthetic apparatus in both bacteria and plants consists of two distinct units called antennae and the reaction centre. Antennae are the light gathering complexes consisting of chlorophyllous pigments as well as carotenoids arranged in the protein matrix. These pigment-protein complexes absorb light and efficiently transfer the excitation to the reaction centre. The reaction centre consists mainly of organic donor and acceptor molecules embedded within a protein matrix. The photosynthetic reaction centre of purple bacteria *Rhodospeudomonas virdis* comprises of four bacteriochlorophylls (BCI), two bacteriopheophytins (BPh), two quinones, namely ubiquinone and menaquinone, and a non-heme iron atom. The spatial arrangement of these components within
the reaction centre is shown in Figure 1.1. It may be noted that with the exception of the iron atom, the constituents occur in pairs and the reaction centre has approximate $C_2$ symmetry. The right side of the $C_2$-axis is known as the L side and the left side is termed M side. Of the four BCl molecules, two are positioned very close. Hence they are strongly coupled electronically and are termed “special pair” of BCl.

The photosynthetic process within the reaction centre begins with the excitation of the special pair BCl by excitation transfer from the antennae units. The singlet excited state of the special pair transfers an electron to the BPh on the L side of the branch within 3 ps leading to the formation of special pair radical cation and BPh radical anion. It is believed that BCI monomer on the L side plays a role in this electron transfer reaction. The M branch of the reaction centre is almost inactive in the electron transfer process. The BPh radical anion decays in 200 ps moving the electron to the menaquinone from where it is further transported to the ubiquinone in about 100 $\mu$s. The positive charge remaining on the special pair is quenched by electron transfer from an iron porphyrin on the outer side of the membrane. The net result of this multistep electron transfer is the generation of a trans-membrane CS state with a quantum yield of near unity. Since the positive and negative charges are separated by the thickness of the lipid bilayer, BET, which leads to the wastage of stored energy, is precluded.
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Figure 1.1. Arrangement of the chromophores, electron donors and electron acceptors in the bacterial reaction centre of *Rhodospeudomonas virdis*

The importance and complexity of electron-transfer reactions in nature has led many researchers to look for ways to duplicate the fundamental features of these reactions in simplified chemical systems. Extremely high quantum yield of the PET processes in the natural systems is attributed to the high degree of organization of the donors and acceptors in the reaction centre. It was believed that some degree of organization could be achieved by covalently linking the donor and acceptor molecules. Considerable effort has been devoted to mimicking the natural photosynthetic process in the laboratory by constructing covalently connected D-A systems and investigating the photoinduced processes in those systems. As is the
case in photosynthetic reaction center, multi-component donor-acceptor arrays that carry out multistep charge separation reactions are found to be very useful for producing long-lived CS states in artificial systems.

1.2. Photoinduced electron transfer in multi-component donor-acceptor systems

It was proposed that efficient and effective charge separation might be achieved by attaching several acceptors to a light-absorbing donor in such a way as to prevent rapid electron return. Suppose three different acceptors A₁, A₂ and A₃ (acceptor strength is in the order A₁ < A₂ < A₃) are attached to the donor D, we would have the sequence of reactions shown in Scheme 1.3, following light absorption by D. Electron transfer is initially favored between D* and A₁ since these groups are closest. Electron transfer then occurs from A₁ to A₂ and then from A₂ to A₃. This process is termed sequential electron transfer. As the charge-separation distance between the ions increases, electron return becomes increasingly difficult, resulting ultimately in long-lived charge separation. A large number of donor-acceptor systems were designed in the past and the electron transfer processes taking place in these systems were studied in detail. Some of these systems are described below.
Mataga and co-workers have investigated the intramolecular PET processes in 1 (Figure 1.2), which consists of a porphyrin connected to two quinones (QA and QB). The CS state lifetime in 1 was 300 ps, which is nearly three-fold of the CS state lifetime (≈100 ps) observed in a dyad consisting of a porphyrin linked to a quinone by four methylene groups.
In this triad, photoexcitation of the porphyrin is followed by a sequential electron transfer:

\[
P \cdot Q_A \cdot Q_B \rightarrow ^1P^* \cdot Q_A \cdot Q_B \rightarrow P^{**} \cdot Q_A^* \cdot Q_B \rightarrow P^{**} \cdot Q_A \cdot Q_B^*
\]

The lifetime of CS state is longer in triad because of the large separation distance between \( P^{**} \) and \( Q_B^* \).

Gust, Moore and co-workers are the pioneers in the design of multi-component arrays to mimic natural photosynthesis. They have investigated PET processes in several porphyrin (P) - quinone (Q) - carotenoid (C) systems. The C-P-Q triad 2 (Figure 1.3) is one of the earliest examples.

![Figure 1.3](image_url)

On the basis of electrochemical and spectroscopic studies PET pathways as shown in Scheme 1.4 were postulated for 2. Initially, photoexcitation of the porphyrin produces its singlet excited state. This step is followed by an electron transfer from singlet porphyrin to the quinine acceptor, to generate C-P^{**} - Q^{*}. A second electron
transfer from the carotenoid to the porphyrin moiety then leads to the formation of long-lived C*-P-Q* state. Using transient absorption spectroscopy the authors identified the carotenoid radical cation absorption at 950 nm, which exhibited a lifetime of few hundred nanoseconds.

Scheme 1.4. Schematic representation of PET processes in C-P-Q triad

The same authors have extended this work to the molecular tetrad 3 (Figure 1.4).
The lifetime measured for the final CS state in 3 was 450 ns, which was considerably larger than that observed for 2. The ET pathways suggested for 3 are shown in Scheme 1.5. The long lifetime of C$^{**}$-P-$Q_A^-$-$Q_B^*$ was ascribed to the large distance separating C$^{**}$ and $Q_B^*$.

Gust, Moore and co-workers have also investigated the PET processes in the C-P-$Q_A$-$Q_B$ tetrad 4 (Figure 1.5) where $P_A$ stands for a zinc porphyrin and $P_B$ for a free porphyrin and Q is a naphthaquinone. The final charge separated state, C$^{**}$-$P_A^-P_B$-$Q^*$ was long-lived (2.9 μs) and was identified by its absorption at 980 nm using transient absorption studies.
The same group has synthesized and studied the electron transfer processes in the molecular pentad C-PA-PB-QA-QB (5, Figure 1.6).\textsuperscript{10} Very efficient PET is found to take place in this system. Transient absorption studies revealed that a CS state, C-PA-PB-QA-QB is formed with a lifetime of about 0.55 μs and an overall quantum yield of 0.83 after the series of sequential electron transfer steps shown in Scheme 1.6.
Several other groups were also engaged in the construction of polyads capable of long-lived charge separation. For example, Wasielewski et al.\textsuperscript{11} have reported a long-lived CS state in triad 6 (Figure 1.7), consisting of a porphyrin bearing a quinone acceptor and a dimethylaniline-based secondary donor. Here a final CS state is formed in 71% with a lifetime of 2.4 $\mu$s.
Flamigni et al. have synthesised and investigated the PET processes in a triad 7 (Figure 1.8), where an Ir (III) bisterpyridine complex connected through an amidophenyl spacer to a triphenylamine electron donor and to a naphthalene bisimide electron acceptor. Steady state and time-resolved optical spectroscopy showed that in this system PET leads to a final CS state with a lifetime of 120 µs. A variety of other successful triads for substantial stabilization of the CS state have been reported in recent years.

Several reports dealing with the construction of higher order tetrads and pentads are available in the literature. Guldi, Imahori and co-workers have achieved extremely long-lived CS states ranging from hundreds of milliseconds to a few seconds in tetrads. For example, tetrad 8 (Fc-ZnP-H2P-C60, Figure 1.9) gave the final CS state Fc\(^{\text{II}}\)-ZnP-H2P-C60\(^{\text{II}}\), which exhibited a lifetime of 380 ms in benzonitrile solution, with a quantum yield of 0.17.
Tetrad, 9 (Figure 1.10) containing Zinc porphyrin (PZn) and methyl viologen (MV$^{2+}$) as the terminal chromophores and dimethoxynaphthalene (DMN) and naphthaquinone (NQ) as intermediate chromophores studied by Paddon-Row et al.\textsuperscript{15} offered very good photoinduced charge separation. 9 exhibited CS state lifetimes of 250-450 ns in different solvents.

Although the construction and use of multi-component polyads for photoinduced electron transfer is successful in generating long-lived CS states, the approach suffers from some serious drawbacks. First of all, the synthesis of multi-component systems is very tedious and time consuming. Hence this is a very expensive process. Another important shortcoming is that a significant amount of
energy is lost during each sequential electron transfer step. As shown in Scheme 1.3, each of the forward ET process is exergonic and hence energy stored in the CS state decreases in every step. The final CS state would have much less energy stored in it compared to the initial CS state. Therefore, even though the lifetime of the final CS state is fairly long enough, the energy associated with it (i.e. the energy available to do useful work) would be very low. Thus, it is highly desirable to design and synthesize simple molecular dyads which are capable of fast charge separation but retain long CS state lifetimes without the energy loss.\textsuperscript{16}

1.3. Photoinduced electron transfer in simple donor-acceptor dyads

Considerable amount of work is reported in the literature regarding photoinduced electron transfer in covalently linked dyad molecules. Initial systems studied comprised of a porphyrin as both the light absorber and electron donor and a quinone as an electron acceptor.\textsuperscript{13a} Other redox components have been proposed, and there now exists a multitude of light active molecular dyads that undergo fast charge separation upon excitation. But almost all such dyads underwent rapid charge recombination, which severely restricted the lifetime of the charge separated state. Indeed, typical lifetimes for the charge separated state in fluid solution are on the order of some hundreds of picoseconds to a few nanoseconds. This range is much too short to carry out useful chemistry with the intermediate
radical ions. Some special approaches are attempted in literature to increase the lifetime of CS ion pairs in simple D-A dyads.

1.3.1. Invoking spin restriction rule for long-lived CS state

One successful approach has been to make the decay of the CS state to the ground state a spin-forbidden process. In particular, this involves the design of dyads in which the CS state has triplet state character ($^3$CS). As will be exemplified below, this allows the creation of CS states with microsecond lifetimes in simple and very compact dyads.

In compact dyads the exchange interaction between D and A in the CS state may be expected to be large enough to allow for discrete singlet and triplet CS states ($^1$CS and $^3$CS). $^1$CS can easily be populated when it is energetically below the lowest locally excited singlet state. $^1$CS can undergo intersystem crossing (ISC) to $^3$CS. If $^3$CS is the lowest triplet level in the dyad, then $^3$CS has to decay eventually to the singlet ground state. This process would be slow because of the spin forbidden nature of this transition, leading to long CS state lifetimes. In general, local triplet states of D and A lie significantly below the $^{1,3}$CS states in non-polar solvents. As the solvent polarity increases, local triplet levels are generally unaffected, but $^{1,3}$CS state energies decrease considerably. Thus would ultimately lead to a situation in polar solvents, where the $^3$CS state would be lower in energy compared to the local triplet levels, as shown in Scheme 1.7.
As shown in Scheme 1.7, few compact dyads can exhibit long-lived charge separation in polar solvents. This approach, however, suffers from two disadvantages. The energy stored in such CS states would be considerably lower compared to the energy absorbed. Secondly, if the ISC efficiency between the singlet and triplet CS states is low, then a considerable fraction of the CS state would be present in the singlet state, which would undergo very fast BET to the ground state. Quantum yield of the CS state would be very low in such a case. Some of the few compact dyads for which long-lived CS has been achieved are
compiled in Figure 1.11, together with quantum yields and lifetimes of their $^3$CS states. A more detailed discussion is presented below.

$$\begin{array}{c|c|c}
\text{Q} & \Phi (%) & \tau (\mu s) \\
\hline
10 & 26-55 & < 2.4 \\
& & \text{(cyclohexane)} \\
11 & \sim 100 & 3.35 \text{ (THF)} \\
& & 1.0 \text{ (CH}_3\text{CN)} \\
12 & " \text{High}" & \\
13 & \sim 30 & >> 0.02 \text{(CH}_3\text{CN)} \\
\end{array}$$

Figure 1.11. Structure of D-A dyads which form long-lived $^3$CS state with quantum yields and lifetimes

While all the systems compiled in Figure 1.11 fulfil the requirement that $^3$CS is the lowest excited state, most probably in polar solvents, the mechanism employed to achieve significant population of $^3$CS after excitation differs from case to case and sometimes has not been established beyond doubt.
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The simplest mode of population of $^3$CS would involve ISC from $^1$CS to $^3$CS. This spin-forbidden process has to compete with the spin-allowed decay of $^1$CS to the ground state. Since, the latter process tends to be rather fast in compact dyads quantum yield of $^3$CS formation is usually low. In fact, the most successful examples of long-lived $^3$CS states populated via ISC from a short-lived $^1$CS state are those occurring in metal–organic complexes in which the heavy atom effect of the metal allows for ultrafast ISC.

The first report of detection of a long-lived $^3$CS state in a fully organic dyad is by Smit and Warman. They observed that 10 (Figure 1.11) gave a long-lived $^3$CS state. In 10 a carbazole donor and a tetrachlorophthalimide acceptor are linked by a short oligomethylene bridge. Earlier investigations had shown that the $^1$CS state of these compounds is formed following excitation of the donor or acceptor chromophore. This $^1$CS state was found to be short-lived (28 ns in cyclohexane falling to 6 ns in 1,4-dioxane), but later investigations revealed the presence of a long-lived $^3$CS state (lifetime in the microsecond range). The quantum yield of the $^3$CS state showed strong solvent dependence. Thus, for $n = 2$, it falls from 52% in cyclohexane to 10% in 1,4-dioxane. This may be taken as evidence that in these systems $^3$CS is mainly formed via ISC from $^1$CS. For systems containing a longer spacer, the $^3$CS quantum yield is less dependent on polarity. Thus for $n = 7$, $^3$CS state yield varied from 55% in cyclohexane to 33% in 1,4-dioxane. It is suggested that for longer spacers $^3$CS can also be formed by ISC.
from local singlet to triplet state followed by ET in the triplet manifold. It should be stressed that these systems are rather unique in the sense that, their $^3\text{CS}$ state is the lowest triplet even in non-polar solvents like cyclohexane. Under these conditions, the CS state is estimated to lie $\approx 2$ eV above the ground state. Other dyads capable of forming long-lived $^3\text{CS}$ states (\textit{vide infra}) almost invariably require a polar solvent to push $^3\text{CS}$ below any local triplet states (Scheme 1.7).

Anglos \textit{et al.} described the interesting rigid dyad \textbf{11}.\textsuperscript{19} Photoexcitation of \textbf{11} in moderate to high polar solvents leads to virtually quantitative population of a long-lived $^3\text{CS}$ state in which an electron is transferred from the strong diaminobenzene donor to the naphthalenediketone acceptor. Convincing evidence was presented to show that after excitation of the acceptor, and before charge separation in the singlet manifold can take place, very fast local ISC ($^1\text{A}^* \rightarrow ^3\text{A}^*$) occurs and is followed by charge separation in the triplet manifold, leading to very high yield of the $^3\text{CS}$ state. Subsequently, a few other compact systems, such as the piperidine-bridged system \textbf{12},\textsuperscript{20} and malachite green lactone \textbf{13},\textsuperscript{21} have been reported in which excitation in polar or semipolar solvents leads to population of a long-lived $^3\text{CS}$ state, although in less than quantitative yield. As far as can be judged from the solvent dependence of the data reported (Figure 1.11), the lifetime of the $^3\text{CS}$ state decreases slightly in more polar solvents and this is attributed to lowering of the energy gap between $^3\text{CS}$ and the ground state.
In short, direct excitation of compact dyads and other compact donor-acceptor systems leads to population of a long-lived $^3\text{CS}$ state only in rare cases. It is relatively easy to design systems that meet the requirement of $^3\text{CS}$ being below all other excited states. However, it turns out to be difficult to suppress sufficiently, at least in compact systems, all other deactivation processes that occur in the singlet manifold in competition to formation of $^3\text{CS}$.

It was shown recently by Verhoeven et al. that this problem can be circumvented by intermolecular triplet sensitization. Thus, on direct excitation via the dimethoxynaphthalene donor chromophore, the rigid dyad 14 (Scheme 1.8) undergoes quantitative charge separation. This yields a $^1\text{CS}$ state which decays with a time constant that varies from a few nanoseconds in non-polar media to less than 10 ps in polar solvents without a trace of $^3\text{CS}$ formation. Addition of the triplet sensitizer benzophenone (BP), which can be excited at longer wavelength than dimethoxynaphthalene, leads to a situation wherein the $^3\text{CS}$ can be reached via the sequence $^1\text{BP}^* \rightarrow ^3\text{BP}^* \rightarrow ^3\text{D}^* \rightarrow ^3\text{CS}$ in polar solvents (D stands for the dimethoxynaphthalene donor). The corresponding energy diagram is depicted in Scheme 1.8.
The lifetime of $^3\text{CS}$ is 1.4 $\mu$s in acetonitrile, whereas $^1\text{CS}$, as populated by direct excitation, lives for less than 10 ps in the same solvent. This demonstrates that this type of spin control can increase the lifetime of CS states for compact dyads by at least five orders of magnitude without significantly degrading the energy content of the CS state (the energy gap between $^1\text{CS}$ and $^3\text{CS}$ in 14 was estimated to be of the order of only 0.2 eV $= 4.6$ kcal mol$^{-1}$).

While intermolecular sensitization appears to provide a new method to populate $^3\text{CS}$ states in compact dyads, the overall quantum yield of this process is limited by the quantum yield of the intermolecular triplet energy-transfer step.
Increasing the latter to unity may require very high dyad concentrations which may not be experimentally accessible. It therefore seems desirable to design compact dyads that incorporate a suitable sensitizer also. The simple system 15 (Scheme 1.9) designed by Verhoeven and co-workers is the first example of such a system. In addition to the dimethylaniline (D) and the nitrobenzene (A) units, 15 contains an aromatic ketone as a triplet sensitizer (S). A relevant energy diagram in polar solvent is shown in Scheme 1.9.

![Scheme 1.9. Structure and energy level diagram (in polar solvent) of 15](image-url)
From these data it appears that after excitation and ISC of the sensitizer chromophore in a polar solvent, sufficient energy is still available to induce electron transfer from D to A in the triplet manifold. This produces a $^3\text{CS}$ state that is lower in energy than all locally excited states. In low-polarity media, this need not be the case. Nanosecond transient absorption spectroscopic studies on 15 in benzene showed no detectable transients. In acetonitrile, however, a long-lived transient was detected that, under deoxygenated conditions, exhibited a lifetime of $0.33\ \mu\text{s}$. The lifetime was reduced to $56\ \text{ns}$ under aerated conditions and hence the transient absorption was attributed to a triplet species. The absorption spectrum of this transient species displayed peaks corresponding to the acceptor radical anion and donor radical cation. Hence 15 was claimed as the first example of a compact dyad that incorporated an intramolecular sensitization step to produce a $^3\text{CS}$ state.

1.3.2. Conformational approach for long-lived CS state

Another approach to increase the lifetime of CS state in simple dyads is the conformational approach. This method proposes that specific conformation of donor and acceptor during the PET process may help the molecule to attain a long lifetime in the CS state. Our group has reported the Ru(bpy)$_3^{2+}$-phenothiazine dyad 16 (Figure 1.12) wherein the D and A moieties are linked by an amide bond.$^{24}$ Steady state and time resolved spectroscopic techniques showed that the electron transfer rates ($k_{et} > 10^8\ \text{s}^{-1}$) in 16 were much faster than those previously reported ($k_{et} < 10^7\ \text{s}^{-1}$) for other linked Ru(bpy)$_3^{2+}$-phenothiazine systems. Nanosecond
laser flash photolysis showed that compared to the previous systems, back electron transfer rates in these systems were about 100 times slower. Transient absorptions assignable to Ru(bpy)\(^{3+}\) and phenothiazine radical cation, having lifetimes about 30 ns were observed for 16. The fast electron transfer after the photoexcitation, was explained by invoking a closed conformation in which one of the bipyridine ligands or the Ru\(^{3+}\) metal centre is spatially very close to the phenothiazine moiety. Same reason is assigned to the retardation of the BET rate. In this closed conformation Ru\(^{2+}\) and phenothiazine radical cation will be near to each other, leading to repulsion between the two positive charge centres, which reduce the BET rate.

![Figure 1.12](image)

1.3.3. Invoking Marcus inverted region effect for long-lived CS state

Another approach to increase the lifetime of the CS state is to design D-A dyads for which BET falls in the Marcus inverted region. In order to understand the conceptual basis of this proposal, a detailed description of the Marcus equation
is required. According to the Marcus theory of electron transfer, the rate constant of non-adiabatic electron transfer \( k_{ET} \) is given by eqn (1.1),

\[
k_{ET} = \left( \frac{2\pi}{h} \right) H_{el}^2 \left( 4\pi \lambda k_B T \right)^{1/2} \exp\left[ -\left( \lambda + \Delta G_{ET} \right)^2 / 4\lambda k_B T \right]
\]

\( h \) is the Planck's constant divided by \( 2\pi \), \( H_{el} \) is the electronic coupling matrix element between the donor and acceptor, \( \lambda \) is the reorganization energy of the electron transfer, \( k_B \) is the Boltzmann constant and \( T \) is the absolute temperature. The reorganization energy of electron transfer \( (\lambda) \) is the energy required to structurally reorganize the donor, acceptor and their solvation spheres upon electron transfer. Depending on the relative values of \( \Delta G_{ET} \) and \( \lambda \), equation (1) envisages three typical kinetic regimes for electron-transfer reactions as shown in Figure 1.13: i) a normal region \( (\Delta G_{ET} < \lambda) \) where electron transfer is thermally activated and is favored by an increase in the driving force, ii) an “activation-less” regime \( (\Delta G_{ET} = \lambda) \) where the rate is maximum, and iii) an “inverted region” for strongly exergonic reactions \( (\Delta G_{ET} > \lambda) \), where the rate actually decreases with increase in driving force. The existence of an inverted region was the most important prediction of Marcus theory. Conclusive experimental evidence for the inverted region was provided in 1984 by Miller \textit{et al}., almost 25 years after it was predicted. Although definitive evidence for its existence was lacking for a long time, the inverted region is now well established in fixed-distance electron-transfer reactions.
Figure 1.13. Schematic representation of a Marcus parabola

Miller and co-workers had proved the existence of inverted region in covalently connected rigid D-A systems. Our group has established the existence of Marcus inverted region in supramolecular dyads such as hydrogen bonded D-A systems and cyclodextrin-encapsulated systems.28,29 Our group was able to demonstrate the whole Marcus parabola on the basis of raw fluorescence lifetime data.29

It has been suggested that one can design dyads exhibiting long-lived CS states with the aid of the Marcus parabola. One can select D-A systems in such a way that the $k_{\text{PET}}$ values lie at the top of the Marcus parabola and $k_{\text{BET}}$ values lie deep in the inverted region. In such a case the forward ET would be extremely fast and the BET would be very slow. In such systems $k_{\text{PET}}/k_{\text{BET}}$ values could be very large ($\geq 10^4$) and it would be possible to observe a long-lived CS state. However,
straight forward demonstration of this “inverted effect” has been very rare. A general observation is that when $\Delta G_{\text{BET}}$ is very large other deactivation channels such as jumps to low lying local triplet levels may prevail over charge recombination to the ground state. Nuclear tunnelling also becomes very important and it is suggested that the Marcus equation may not adequately describe electron transfer in the deep inverted region. There are, however, several papers which claim long-lived CS state formation due to the inverted effect. Since this thesis deals with long-lived charge separation due to inverted region effects, a detailed description of these papers is given below.

Our group has studied the PET between anthracene attached to a $\beta$-cyclodextrin (17, Figure 1.14) and pyromellitidiiimide (18) in aqueous solution. In aqueous solution 18 would be encapsulated into the $\beta$-CD cavity, as confirmed by UV-Visible absorption, induced circular dichroism, $^1$H NMR, cyclic voltammetric and fluorescence studies.
Photoinduced electron transfer in the system was studied by fluorescence quenching and laser flash photolysis techniques. At higher concentrations of \textit{17}, it was found that the equilibrium was largely in favour of the supramolecular complex between \textit{17} and \textit{18} and intra-ensemble PET was found to take place. The rate constant for electron transfer within the ensemble from the singlet excited state of anthracene was measured. The experimentally determined rate constant agreed very well with that calculated using the Marcus equation. It was observed that a fraction of the charge separated ion pairs survived for more than 200 \(\mu\text{s}\) and this was attributed to inverted region effects.\textsuperscript{30}

Inverted region effect was also invoked to explain long-lived charge separation in the covalently linked D-A system \textit{19} (Figure 1.15), studied by Lambert \textit{et al.}\textsuperscript{31}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure115.png}
\caption{Figure 1.15}
\end{figure}
Electrochemical and fluorescence studies indicated the possibility of very efficient PET with a quantum yield of near unity. Transient absorption spectroscopy showed that a fraction of the charge separated state has a lifetime of 1.7 μs. It is assumed that both singlet and triplet CS states contribute to the transient absorption. Considering the very low reorganisation energy of the system, BET from both the \(^1\)CS and \(^3\)CS state would be in the Marcus inverted region. In addition, BET from the \(^3\)CS to the singlet ground state would be spin forbidden and slow. It was claimed that the system exhibited a long lifetime for the CS state due to a combination of both inverted region effects and spin-selection rules.

In order to see long-lived charge separation it is essential that the CS state energy be lower than the triplet excited state energies of the donor and acceptor components of the dyad. Otherwise, the CS state would decay rapidly to the triplet excited state rather than to the ground state in the Marcus inverted region. Therefore porphyrin and fullerene derivatives which have local triplet states above the CS state would be ideal components in designing simple molecular dyads capable of long-lived charge separation. Also, the inherently low inner sphere reorganization energy of fullerene and porphyrin/chlorin systems makes the BET process in these dyads to fall in the inverted region.

Fukuzumi and co-workers were among the first to design simple donor acceptor systems based on fullerene and porphyrin/chlorine components which
exhibited long-lived CS states. The system designed (20, Figure 1.16) consisted of zinc chlorin as the donor and fullerene as the acceptor.\(^\text{32}\)

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{20.png}
\caption{Figure 1.16}
\end{figure}

Nanosecond laser flash photolysis gave absorptions corresponding to the zinc chlorin radical cation and fullerene radical anion. The peaks corresponding to the CS state decayed via first order kinetics with a lifetime of \(\approx 110\ \mu\text{s}\). Formation of the long-lived CS state is further confirmed by ESR spectroscopy. Irradiation of 20 in PhCN at 143 K gave two characteristic ESR signals, one of which is attributable to an organofullerene radical anion (small \(g\) value) and the other to the chlorin radical cation (higher \(g\) value).

Fukuzumi \textit{et al.} have designed another dyad, 21 with zinc-imidazoporphyrin as the donor and fullerene as the acceptor (Scheme 1.10).\(^\text{33}\)
Excitation of 21 led to the formation of a CS state with 260 μs lifetime at 298 K. At 278 K, the lifetime of the CS state was 310 μs. Energy level diagram (Scheme 1.10) reveals that the CS state (1.34 eV) is lower in energy than the triplet excited state of both C\textsubscript{60} (1.50 eV) and zinc-imidazoporphyrin (1.36 eV). In this case also long lifetime of the CS state is attributed to the inverted region effect.

Fukuzumi et al. designed dyad 22 (Figure 1.17), which is a modification of 20. Here the zinc chlorin donor is attached to the fullerene acceptor through an extremely short rigid linkage.\textsuperscript{34} According to Marcus theory, a smaller distance between the donor and acceptor moieties leads to a reduction in the solvent reorganization energy. Hence the reorganization energy \( \lambda \ll -\Delta G^0_{\text{BET}} \), and this will push BET in the system deeper into the inverted region. The absorption spectra of the compound indicated that there is no significant electronic interaction between the individual chromophores in the ground-state despite the short linkage.
separating them. Fluorescence lifetime of 22 (10 ps) was significantly reduced compared to that of unlinked zinc chlorine (2.7 ns) as a result of electron transfer from the singlet excited state of the zinc chlorin to the C$_{60}$ moiety of the dyad. The rate constant of electron transfer from singlet excited state of the zinc chlorin to C$_{60}$ was determined as $1.0 \times 10^{11}$ s$^{-1}$. Transient absorption spectrum of 22 showed the formation of fullerene radical cation and zinc chlorin radical anion (Figure 1.17). The quantum yield of the CS state formation was 12%, which is smaller than the fluorescence quenching efficiency (99.6%). The authors explained this by invoking a short-lived exciplex state, only a part of which is converted into the long-lived CS state (Figure 1.10).

![Figure 1.17. Structure of the dyad 22 and its transient absorption spectrum](image)

The CS state decays by back electron transfer to the ground state rather than to the triplet excited state since the CS state is lower in energy (1.26 eV) than both the triplet excited states of C$_{60}$ (1.50 eV) and zinc chlorin (1.36 - 1.45 eV). $k_{\text{BET}}$
obtained for 22 was $4.2 \times 10^3$ s$^{-1}$, corresponding to a CS state lifetime of 230 $\mu$s at 25 $^\circ$C. ESR spectroscopy also gave evidence for the formation of long-lived charge separation. Lifetime of the CS state showed large temperature dependence indicating that the BET process belongs to the deep inverted region. The lifetime of the CS state at -150 $^\circ$C is as long as 120 s, which is the longest CS lifetime reported for linked D-A systems with porphyrin and fullerene derivatives as components.

A major disadvantage of chlorine-C$_{60}$ systems is the very low energy of the CS state (1.2 – 1.3 eV). In the case of the porphyrin-C$_{60}$ systems the low triplet energies of porphyrins have precluded attempts to attain long-lived CS states with a higher energy than the triplet energies. In such a case, it is highly desirable to have a chromophore which has high triplet energy and small reorganization energy. Acridinium ion is a good candidate for such a purpose, since the reorganisation energy (0.3 eV) for the electron self-exchange between acridinium ion and the corresponding one-electron reduced radical is the smallest among redox active organic compounds. The triplet energy of acridinium ion is also very high.

Fukuzumi et al. have designed the dyad, 9-mesityl-10-methylacridinium ion, (23, (Acr$^+$-Mes), Figure 1.18), in which the electron donor moiety (mesityl group) is directly linked to the 9-position of acridinium ion. Because of the very short distance between the D and A moieties the solvent reorganization energy for
the electron transfer will be minimized in 23. The X-ray crystal structure of Acr⁺-Mes indicated that the donor and acceptor moieties are perpendicular to each other and that there is no orbital interaction between the two. Indeed, the absorption and fluorescence spectra of Acr⁺–Mes are superpositions of the spectra of the components, i.e., mesitylene and 10-methylacridinium ion. The energy of the CS state (Acr⁺–Mes⁺⁺) is determined by the redox potentials of the components and the value obtained was 2.37 eV. \( \Delta G^0 \) for PET in 23 was -0.31 eV.

![Figure 1.18](image)

Photo-irradiation of a deaerated solution of Acr⁺–Mes in acetonitrile by a nanosecond laser light flash at 430 nm resulted in the formation of a transient in 98% yield. Based on several experiments the authors assigned the transient absorption to the CS state Acr⁺–Mes⁺⁺, formed as a result of electron transfer from the mesitylene moiety to the singlet excited state of the acridinium ion moiety. The transient was found to be very long-lived with a lifetime of about 2 h at 203 K. BET in the CS state was too slow to compete with the intermolecular BET reaction as evidenced by the decay time profile of Acr⁺–Mes⁺⁺, which obeyed second-order
kinetics. In contrast, the decay of the CS state obeyed first-order kinetics in benzonitrile at high temperatures. This indicates that the rate of the intramolecular BET of the CS state becomes much faster than the rate of the intermolecular BET at higher temperatures because of the larger activation energy of the former than the latter. When the irradiation was performed at low temperatures, the colour of the sample changed from green to brown. The resulting solution afforded the absorption spectrum due to the CS state, which consisted of the absorption bands of the Acr* and Mes** moieties. No decay of the absorption due to the CS state was observed. This observation prompted the authors to claim an almost infinite lifetime for the CS state Acr*-Mes** at 77 K. EPR experiments also gave evidence for the formation of long lived CS state. The authors claimed that formation of such a remarkably stable CS state is made possible by the high energy of the CS state (2.37 eV), which is located deeply in the Marcus inverted region. It is also claimed that the CS state could undergo secondary electron transfer experiments with donors such as anthracene and acceptors such as naphthalenediimide or methyl viologen. Because of the long CS state lifetime the authors used 23 as photoredox catalyst in various applications.

Another simple D-A dyad, 24 (Figure 1.19) reported by the same group consisted of a formanalide moiety as the donor and anthraquinone moiety as the light absorber and triplet-state electron acceptor. The one-electron oxidation and reduction potentials of 24 were determined by cyclic voltammetry and second
harmonic AC voltammetry as 1.37 V and -0.87 V vs SCE, respectively. The driving forces for the PET and BET were calculated to be -0.21 and -2.24 eV, respectively. Energy of the CS state is found to be less than all local singlet and triplet energies in 24.

Femtosecond transient absorption studies showed that, upon photoexcitation of 24 in DMSO, electron transfer takes place from the formanilide to the triplet state of anthraquinone within 1.7 ps. Nanosecond laser flash photolysis gave a transient with 900 μs lifetime. Based on evidence from secondary electron transfer experiments the authors assigned the long-lived absorption to the CS state. In this case also, long lifetime of the CS state was attributed to the inverted region effects.

Harriman, Verhoeven and co-workers have questioned the claims made by Fukuzumi et al. regarding the formation of long-lived CS states in 20, 21, 22, 23 and 24. They have reinvestigated the photophysical processes taking place in these systems and came up with alternate interpretations. According to them the formation of long-lived CS state due to inverted region effects is not possible in any of these systems.
According to Harriman, Verhoeven and co-workers the energy level diagram for 22 is as shown in Scheme 1.11. According to them, the energy levels of 22 fulfil the requirements discussed earlier for dyads capable of forming long-lived $^3$CS state, since no local triplets are situated below the $^3$CS state. Therefore, an alternative explanation for the reported observations may readily be proposed, at least as far as the behaviour in liquid solution is concerned. According to these authors, the short-lived “exciplex” species that Fukuzumi et al. invoked could actually be the $^1$CS, of which apparently 88% decayed to the ground state and 12% underwent ISC to a longer lived $^3$CS state. If the CS state has triplet character, inverted region effects need not be invoked and long lifetime of CS state could be attributed to spin restriction factors on charge recombination.

![Energy level diagram proposed for dyad 22](https://example.com/diagram.png)

Scheme 1.11. Energy level diagram proposed for dyad 22

According to Harriman, Verhoeven and co-workers the EPR signal observed in the photo-irradiation of 22 may be resulting from separate radical ions residing on
different molecules. If so, the temperature-dependent EPR lifetime data reported for 22 can no longer be considered as proof for a strongly temperature dependent $k_{\text{BET}}$. Harriman, Verhoeven and co-workers thus concluded that the long-lived CS state formed in 12\% yield on the photolysis of 22 in solution is the $^3\text{CS}$ state and there is no need to invoke the inverted region effect to explain the long lifetime. The same seems to apply to related dyads, 20 and 21.

Fukuzumi et al. have claimed that 23 is even better than the natural photosynthetic system both in terms of the amount of energy stored and lifetime of the CS state. They initially estimated the energy of CS state in 23 at 2.37 eV. But investigations by Harriman, Verhoeven and others suggested that the CS state is at 2.57 eV, which is barely below $^1\text{(Acr}^+)^\ast$ (2.67 eV). They were also successful in obtaining the phosphorescence spectrum of 23, which placed the lowest $^3\text{(Acr}^+)^\ast$ energy at 1.94 eV above the ground state. Based on all these observations they have constructed the energy level diagram of 23 as shown in Scheme 1.12. Harriman, Verhoeven and co-workers argue that $^3\text{(Acr}^+)^\ast$ lies below the $^1\text{CS}$ level and hence the $^1\text{CS}$ state would cross over to $^3\text{(Acr}^+)^\ast$ and the transient that Fukuzumi et al. observed is actually $^3\text{(Acr}^+)^\ast$. 
According to Harriman and Verhoeven, the $^3(Acr^+)^*$ state is a poor reductant and hence incapable of reducing dialkyl naphthalenediimide or viologen dication. These authors attributed the secondary ET reactions of 23 (reported by Fukuzumi et al.) to reactions of either $^3(Acr^+)^*$ or the radicals derived via chemical decomposition of Acr$^*$-Mes$^{**}$. According to Harriman, Verhoeven and co-workers, the overall photophysics and photochemistry of 23 follow quite usual pathways known for many related systems and certainly do not require the involvement of any excited state with unusual properties. Studies by these authors on 23 indicated that the CS state has a lifetime of only 6 ns at room temperature. During the last five years, Fukuzumi et al. published several papers supporting long-lived CS state in 23 and...
Harriman, Verhoeven and co-workers published several papers opposing this claim. It must be stated here that photoinduced electron transfer in 23 remains a controversial topic even today.

In the case of dyad 24, the femtosecond laser flash photolysis experiment by Fukuzumi *et al.* showed that this dyad undergoes very fast ($\tau_{\text{ISC}} = 0.4$ ps) ISC before charge separation occurs. There thus seemed to be no doubt that the CS state in 24 must be born with a triplet spin multiplicity, and it can be assumed that this might be an important factor in slowing down its recombination to the singlet ground state by intramolecular electron transfer. However dyad 24 had been investigated earlier by others who reported no evidence for the formation of a long-lived CS state in this molecule$^{41}$. Harriman, Verhoeven and co-workers therefore synthesized and reinvestigated the PET processes in 24.$^{40b}$ Their study confirmed the earlier reports that no long-lived CS state is formed in common solvents such as acetonitrile or benzonitrile. However, in the DMSO solvent employed by Fukuzumi and co-workers, very long-lived transients were observed with a spectrum closely matching to that of the anthraquinone radical anion. It was suggested that the anthraquinone radical anion was formed as a result of ET between triplet state of anthraquinone moiety and DMSO solvent which acts as a sacrificial electron donor. In fact, several anthraquinone derivatives including 9,10-anthraquinone itself, were capable of photo-oxidizing DMSO. Based on these observations Harriman and Verhoeven dismissed the claims of long-lived CS state
in 24. In subsequent papers Fukuzumi et al. have rebutted all the findings by Harriman, Verhoeven and others and the PET processes in 24 is also an unsettled issue at present.

1.4. Origin of the present work

The most important aspect of Marcus theory was the prediction of an inverted region in electron transfer reactions. This aspect of Marcus theory was controversial from the time the theory was proposed in 1956 until John Miller's group at Argonne National Laboratory found experimental proof for it in 1986. Though long controversial, the presence of inverted region kinetics is now well established in a large number of charge shift and charge recombination reactions. In these examples, the forward PET reaction was generally restricted to the normal region and BET was restricted to the inverted region. Our group were among the first to establish the occurrence of the inverted region in PET reactions and considerable amount of work was carried out previously in our research group in this area.28-30

As mentioned earlier the presence of the inverted region is firmly established in several BET reactions.13(a)42 In almost all these cases, however, the slowest rate observed in the inverted region was \( \geq 10^8 \text{ s}^{-1} \). In the light of these observations claims of \( k_{\text{BET}} < 10^4 \text{ s}^{-1} \) from the Fukuzumi group is to be viewed with suspicion. It has been suggested that when \(-\Delta G_{\text{BET}}\) is very large other deactivation
channels such as jumps to low lying local triplet levels may prevail over charge recombination to the ground state. Nuclear tunneling also may become very important and it is suggested that equation 1.1 may not adequately describe electron transfer in the deep inverted region. When viewed from this angle, the arguments of Harriman and Verhoeven seem reasonable.

The concept of designing dyads capable of long-lived charge separation due to the inverted region effects, however, seems very attractive. Theoretically, such a finding would reaffirm the existence of the inverted region. From a practical point of view, the time and effort required for the synthesis of complex tetrads, pentads etc can be saved. Loss of energy in sequential electron transfer steps can also be avoided. In this thesis an attempt is made to design dyads capable of long-lived charge separation. It is clear from the discussion in section 1.3 that most compact dyads would possess low lying local triplets below the CS state and this aspect is responsible for the absence of long-lived charge separation in dyads. We reasoned that if we choose chromophores with extremely high fluorescence quantum yield (or extremely low ISC efficiency), then we might be able to circumvent this difficulty. In these systems ISC to low lying local triplet levels would be slow or absent leading to long lifetimes for the CS state due to inverted region effects. In the remaining chapters of this thesis this idea is demonstrated and discussed in detail.
1.5. References


20. van Dijk, S. I.; Groen, C. P.; Hartl, F.; Brouwer, A. M.; Verhoeven, J. W. J. 


