Solvatochromism, Aggregation and Photochemical Properties of Fullerenes, C_{60} and C_{70}, in Solution

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Fullerenes, C_{60} and C_{70}, display interesting physicochemical properties in solutions, especially due to their unique chemical structures and their good electron accepting abilities. Solubility of fullerenes in different organic solvents and their unusual solvatochromic behavior, the ability of the fullerenes to form aggregates in solutions, and their electron transfer and charge transfer interactions with variety of electron donors, are the subjects of extensive research activities for more than one decade. Many research groups including ours have contributed substantially in the understanding of the solvatochromism, aggregation behavior, and the photoinduced electron transfer and charge transfer chemistry of fullerenes, in condensed phase. Present article is aimed to summarize the important results reported on the above aspects of fullerenes, subsequent to the earlier report from our group (*D.K. Palit and J.P. Mittal, Full. Sci. & Tech. 3, 1995, 643-659*).

INTRODUCTION

Since the separation of the fullerenes, C_{60} and C_{70}, in macroscopic quantities from the soots [1], extensive studies have been carried out on the scientific and technological importance of these molecules. The interests in studying the fullerenes are of two folds. Firstly, to understand the behaviour of fullerenes in solution and consequently their chemical properties. Secondly, to explore the use of fullerenes and their derivatives as noble materials [2]. Due to their unique molecular structures, fullerenes display unusual behaviour not only in their solvatochromism but also in their chemistry. Fullerenes and their derivatives have been indicated to have many potential applications in diverse fields. A very recent result shows that C_{60} can be used as high temperature (117 K) superconductor [3]. Rational synthesis of C_{60} from simple organic molecules (chlorobromobenzene) [4] may further encourage research in the fullerene chemistry.

Fullerenes are only allotrope of carbon, which are soluble in several organic solvents and behave like many other organic molecules [5,6]. The vibrant colors of fullerenes, C_{60} and C_{70}, in solutions, their excellent electron accepting properties, and high yields of singlet oxygen on their photo-excitation have generated tremendous interest in the study of their photophysical and photochemical properties [7-9]. It was soon realized that the fullerenes rather than acting as three-dimensional aromatic molecules, behave more like conjugated molecules and act as good electrophiles [10]. The

exotic three-dimensional structure of fullerenes with spherical hollow cage is responsible for their extraordinary behavior in solution. Their ability to act as electron relays and to generate long lived excited states has made them an important class of photochemically active compounds. What started as a curiosity to study these exotic caged spherical molecules containing five and six membered rings with good electron density, so called 'Bucky balls' in early days, has now grown in to a full-fledged research field [7,8,11,12]. Very few chemical species have attracted such a divergent attention of the scientific community as have been made by the fullerenes. Bucky ball has rightly been named as the "*molecule of the year*" in 1991 by *Science* [13].

Photochemistry of fullerenes, especially C_{60}, is very attractive mostly due to the relatively low energy gap between the lowest excited singlet and triplet states (~5.5 kcal/mol), which gives rise to efficient intersystem crossing (ISC) process, resulting high yield of its triplet state (>95%) [14,15]. Photoinduced electron transfer processes involving fullerenes have been studied with vigour in order to find out material for applications in systems like solar cells [16]. Photoinduced reactions of fullerene are also being pursued for developing synthetic routes to new fullerenes [17,18]. Photoinduced generation of singlet oxygen in high yields has fuelled the use of fullerenes in applications like photodynamic therapy [9,14,15].

In this article our endeavor is to summarize two important aspects of fullerenes namely: 1) solvatochromism and the aggregation behaviour of these molecules in solution and 2) importance of fullerenes in photoinduced electron transfer reactions involving charge separation and charge recombination processes. Present article mostly summarizes the results reported in the above aspects from our laboratory subsequent

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to the earlier review from our group in 1995 [19] and includes a concise account of the relevant reports from other research groups.

DISCUSSION

Solvatochromism

The interest in studying the behaviour of fullerenes in solution is motivated by the fact that the fullerene is the only existing allotrope of carbon, which is found to be soluble in various organic solvents [20,21]. The peculiarity of fullerenes is due to their unique spheroidal molecular structures, distinct from the other carbon allotropes, with no sharp edges and dangling bonds. Because of the fact that the intermolecular interaction between two fullerene molecules in crystalline state is very weak, the dissolution of fullerenes in many organic solvents is found to be quite reasonable.

Numerous investigators have noted extraordinary solvato-chromism in their studies on the electronic spectra of fullerenes in different solvents [22-28]. It is proposed that solvatochromism of fullerenes partly arises due to the electrophilic nature of these molecules, which facilitate the formation of both ground and excited state complexes with π electron donating aromatic solvents. Thus, fullerenes are seen to be more soluble in aromatic solvents than in other solvents. Since in fullerenes the transitions to the lower excited singlet states are forbidden by dipole selection rules based on the high molecular symmetry, the symmetry breaking mechanisms arising out of environmental effects seem to have dramatic spectroscopic consequences. Two types of such effects have been recognized in relation to the electronic transitions in fullerenes: 1) intramolecular effect (e.g. Jahn-Teller distortions, Herzberg-Teller vibronic couplings, etc.) and 2) intermolecular effect (e.g. complex formation, aggregation, solvatochromism, etc.). The solute-solvent inter-actions are expected to have a significant role in the photo-chemisy of fullerenes, because the surface of the fullerene molecules is a strained π orbital system, consisting of sp^2 orbitals with enhanced s character. Some important results on fullerene solvatochromism are discussed below.

Systematic quantitative studies for spectral shifts in electronic spectra of $C_{60,}$ and C_{70} have been reported by Renge and Catalan [23,24,27]. These authors tried to correlate the solvent dependent red shifts in the absorption spectra with the polarizability parameters of the solvents based on their refractive indices [23,24,27]. Catalan showed that there are two distinct patterns in the absorption spectra of C_{60} in mono-substituted benzenes with variable electron donating and withdrawing ability of the substituents [24]. In one type of solvents the C_{60} solution shows a broad band centered at ~550 nm, with a minimum at ~440 nm. In the other type of solvents the C_{60} solutions do not show characteristic minima at ~440 nm. In their study of fifty two odd solvents of different types, they have reported the spectral characteristics of the C_{60}

solutions without giving any suitable explanation to rationalize the observed results. [24]. Contrary to Renge and Catalan, Gallaghar *et al.* have considered that the spectral shifts observed for C_{60} solutions in benzene derived aromatic solvents are related to the solvent-solute π–π stacking, resulting in the stabilization of C_{60} and its excited states [25]. Bensasson *et al.* have attempted to make a correlation for shifts of 330 nm absorption band of C_{60} in polar, non-polar, aromatic and micellar solutions based on solvent dielectric and polarizability parameters [29]. Their results show a quantitative dependence of the spectral red shifts with the solvent polarizability parameter, but no such systematic dependence has been found for the polarity parameter based on the dielectric constants of solvents. The effect of solvents on the electronic absorption and Raman spectra of fullerenes, have been recently reviewed by Armstrong *et al.* [30]. The work outlines how the surface/solvent interactions involving fullerenes affect their physical properties and solvatochromism.

Recently the time resolved absorption spectra of C_{60}-benzene solution has been reported in the near IR region (700–1340 nm) on excitation with 532 nm picosecond pulse [31]. A broad band absorption with a peak at ~970 nm has been observed and claimed to be the first observation of the clear absorption peak of the fist excited singlet (S_1) of C_{60} i.e. $^1C_{60}^*$. We have reported the absorption spectra of $^1C_{60}^*$ in different organic solvents like, benzene, toluene, decalin etc., showing the absorption band is centered at 900 nm [32]. Sasaki *et al.* [33] have investigated the absorption spectra of C_{60} in the ground and excited singlet (S_1) states in twelve different solvents in the wavelength region 560–1190 nm. The absorption spectra observed for $^1C_{60}^*$ immediately after 532 nm excitation have been found to be solvent dependent. The spectral shapes were found to correlate well with the ionization potentials of the solvents rather than the dielectric constants or refractive indices of the solvents. The early time spectra of C_{60} in the solvents of low IP were extraordinarily broad as compared to those in solvents with high IP's.

Unusual colour change, first observed by Sun and Bunker in their studies on the solution of C_{70} in toluene-acetonitrile solvent mixtures, has been rationalized assuming aggregation of C_{70} in these solutions. The solvatochromism of fullerenes in many other solvents and solvent mixtures are also reported to be arising due to the aggregation of fullerenes in solutions [25,32]. Recent results on fullerene aggregations are summarized in the following section.

Aggregation of fullerenes and photochemical behavior of the aggregates

Extraordinary physico-chemical behaviour of fullerenes in solution is related, on the one hand to their exotic structures and on the other hand to the possibilities of the cluster formation of these molecules in solution. As the intermole-cular interaction energy between two fullerene molecules and between a fullerene and a solvent molecule are quite close in

magnitude, fullerenes in solution display a tendency to form aggregates. Such aggregates are expected to have exciting non-linear optical properties, optical switching behaviour and also would be of interest from photodynamic therapeutic point of view.

The unusual color changes for C_{70} solution were first observed by Sun and Bunker [25] in toluene and acetonitrile mixtures and attributed to the formation of aggregates of C_{70}. Photophysical studies provide useful diagnostic tool to investigate the aggregation properties of molecules. The aggregation behavior of both C_{60} and C_{70} has extensively been studied in our laboratory by using absorption, fluorescence and dynamic light scattering techniques in a variety of solvents and solvent mixtures [34-36]. Ying *et al.* [37] have indicated the presence of aggregates of C_{60} in benzene solutions (>1 mM). Using both dynamic and static light scattering (DLS and SLS) techniques, the authors have concluded that on keeping benzene solutions (>1 mM) for more than a month, the slow aggregation of C_{60} gives particles of size ~16 nm. However, these aggregates are found to be very unstable even towards mechanical shaking. Martin *et al.* [38] have reported clusters of C_{60} in solid state with aggregation numbers up to 55. Rudalvige *et al.* [39] have observed an irreversible aggregation of fullerenes in benzene and the aggregation process takes several days. A radical mechanism has been proposed on the basis of the radical scavenger studies.

We have studied the aggregation behavior of C_{60} and C_{70} in various binary solvent mixtures by different optical techniques [34-36]. The absorption spectrum of C_{70} in toluene-acetonitrile (AN) mixtures show additional features when the AN composition exceeds ~60% [34]. A strong band appears in the 550−900 nm range, whereas the fine structures of the C_{70} absorption spectra in the range 300−400 nm essentially disappears. The absorption spectra of both C_{60} and C_{70} undergo considerable changes as a result of solvent and solute concentration changes. The excitation and fluorescence spectra also show considerable changes with the solvent compositions. The changes in the optical properties have been attributed to the formation of fullerene aggregates and further confirmed by the light scattering studies.

Stable aggregates of fullerenes in neat solvents like in benzonitrile (BZN) and benzyl alcohol (BZA) have been reported for the first time from our laboratory [32,35]. Interestingly, it has been observed that below the C_{60} concentration of ~100 μM in BZN, the absorption spectral characteristics do not change with the C_{60} concentration. Where as, above ~100 μM, the absorption spectra changed drastically with the C_{60} concentration. DLS studies show the presence of particles of size ~250 nm in these C_{60} solutions. The absorption spectra of C_{60} in BZN in the concentration range of 1−360 μM are shown in Figure 1A. It is seen that up to a concentration of ~100 μM, the spectra match well with those in solvents like benzene (BZ), toluene (TL) and
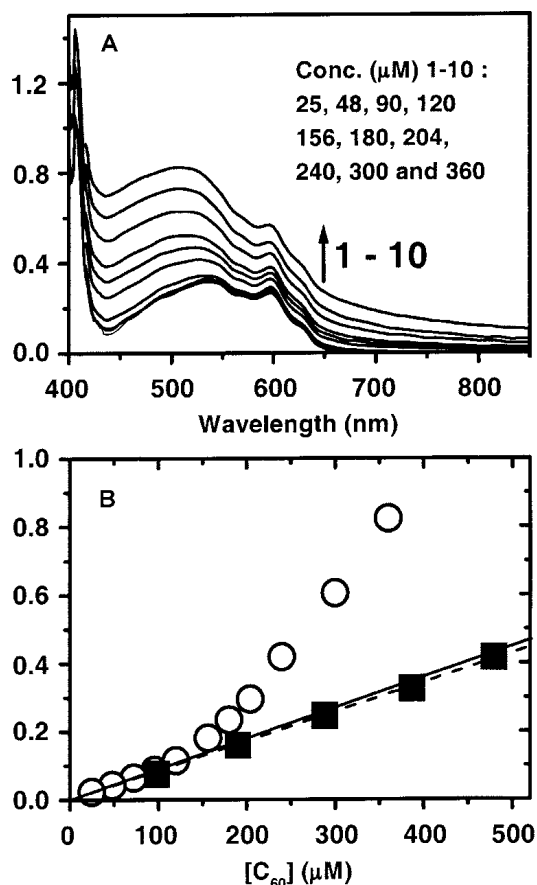

Figure 1. (A) Optical absorption spectra of C_{60} in benzonitrile solution at different C_{60} concentrations. All the spectra are plotted after normalization to the highest concentration of C_{60} used (360 μM). (B) Lambert-Beer plot for the ground state absorption of C_{60} in benzonitrile (○) and decalin (■). Solid line indicates the initial slope for the benzonitrile data. Dashed line shows the linear fit to the decalin data. The observed linearity for the decalin data indicates that the C_{60} remains as the monomers in the solution at all the concentrations used.

decalin (DL), the representative solvents for the unaggregated fullerene solutions. Above ~100 μM of C_{60}, the spectra in BZN solution show blue shift in the 536 nm peak, enhancement in the relative absorbance, decrease in the depth of the valley at ~400 nm, and the appearance of a long wavelength absorption tail extending beyond ~900 nm. A clear break in the absorption vs. concentration plot (Figure 1B) at about 100 μM concentration indicates the changes in the nature of the absorbing species in this solution with C_{60} concentration. No such break is seen in benzene and decalin solutions, indicating the presence of single absorbing species in these solvents. Such changes in the absorption spectra in BZN have been attributed to the aggregation of the fullerene in the solution [32]. The aggregation is confirmed by both DLS and scanning electron microscopy (SEM) measurements [32]. A typical particle size distribution observed by DLS studies, displaying average particle size of ~250 nm and a SEM micrograph obtained
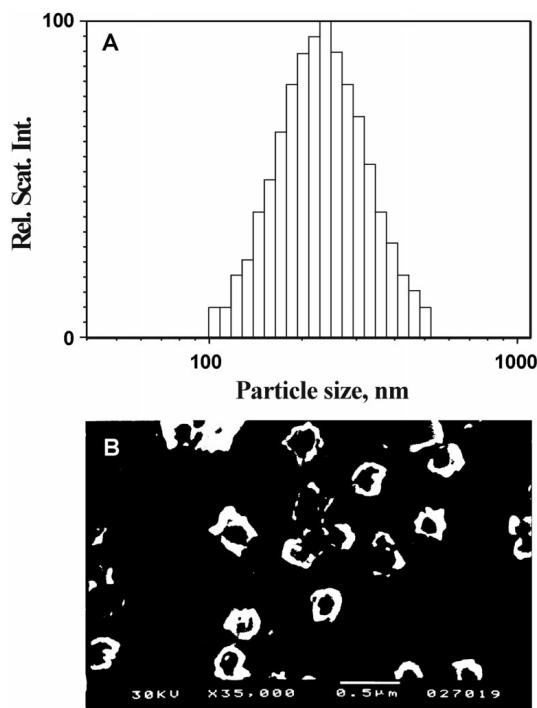
Figure 2. (A) Typical histogram obtained in the DLS experiments for 400 µM C_{60} solution in benzonitrile and (B) typical microgram obtained in the SEM measurements for the microfilms prepared from a 350 µM C_{60} solution in benzonitrile.

from C_{60} solution in BZN is shown in Figure 2. These results indicate that a critical concentration of ~100 µM is required for the formation of C_{60} aggregates in BZN. Similar observations have also been made using BZA as solvent, where below ~200 µM of C_{60} no aggregation has been observed. Below ~200 µM, the spectra of C_{60} in BZA match well with those in low dielectric constant solvents like benzene, toluene, decalin etc [35]. Above 200 µM, however, the spectral characteristics change exactly in the similar manner as observed for C_{60} in BZN solutions beyond a concentration of ~100 µM. Both DLS and SEM studies confirmed the formation of stable aggregates of C_{60} in both BZN and BZA.

The optical absorption changes discussed above are seen to be reversible in nature. This is indicated from the fact that the ground state absorption spectra for the solutions in BZN and BZA containing the C_{60} aggregates revert back to that of the monomers just on dilution. The monomers and aggregates of C_{60} thus coexist in equilibrium and the aggregation process can be represented as,

$$n\,C_{60} \underset{}{\overset{K}{\rightleftharpoons}} (C_{60})_n \qquad (1)$$

The equilibrium constant (K) and the aggregation number (n), however, could not be estimated due to the overlapping monomer and aggregate absorptions and also due to the scattering contributions in the observed spectra.

Interestingly it is seen that the addition of a small amount of

BZ to BZA solutions containing the C_{60} aggregates, the latter disappear. However, for BZN solution containing the C_{60} aggregates, a reasonably high quantity of BZ is required to add to make the aggregates to disappear. These results thus indicate that solvent polarity plays a significant role in the aggregation process of C_{60} in solution. Since BZA is just a moderately polar solvent (ε~13.1), the addition of small amounts of BZ appears to make the solution less polar than required for the aggregate formation. Since BZN is a higher polarity solvent (ε~25), a substantial amount of BZ should be added to reduce the solvent polarity below that required for the fullerene aggregation. Hence, the role of solvent polarity on the formation of C_{60} aggregates has been studied in detail by us. A variety of solvent mixtures have been chosen for these studies, e.g. aromatic-aromatic, aromatic-nonaromatic, nonaromatic-nonaromatic solvent mixtures [35]. The ground state absorption studies in these solvent mixtures shows that in lower polarity solvents the fullerene always remain as monomers, where as in higher polarity solvents the fullerene undergo the aggregation process. It is seen that a critical solvent polarity is required for the aggregation of C_{60} in solution.
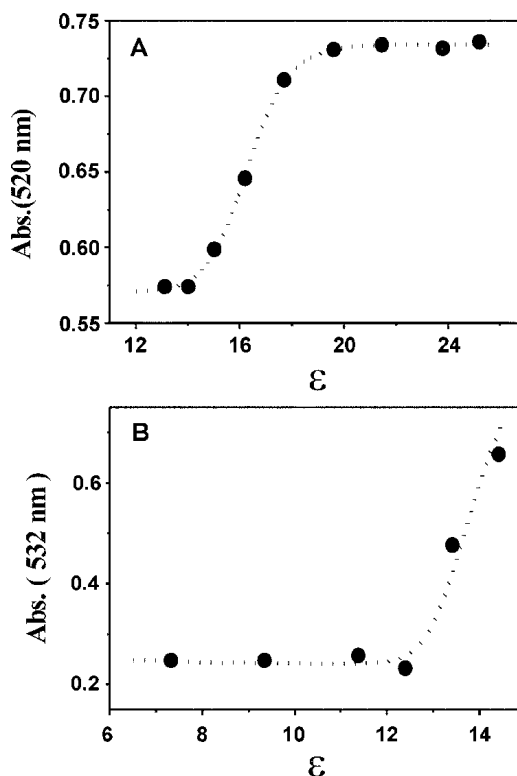
Figure 3. Plots for the absorbances of the C_{60} solutions versus the dielectric constant (ε) of the solvent mixtures: (A) benzonitrile-decalin solvent mixture with $[C_{60}]$=500 µM, measured at 520 nm, and (B) decalin-acetone solvent mixture with $[C_{60}]$=300 µM, measured at 532 nm. The sudden absorbance changes above ε~13 indicate the aggregation of C_{60} in the solutions. The saturation of the absorbance in (A) at higher ε values indicates a complete conversion of the monomeric C_{60} into aggregates.
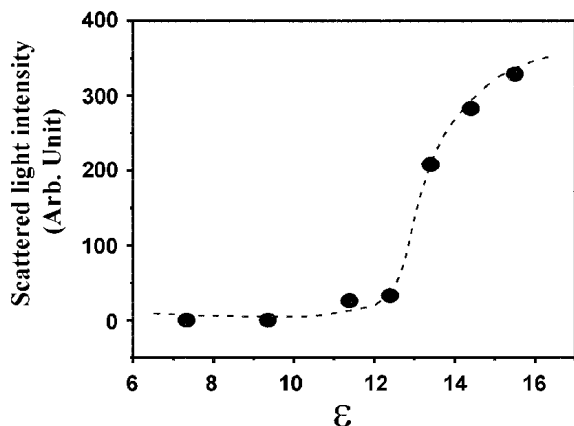
Figure 4. Typical plot for the DLS intensity versus the dielectric constants (ε) of the solvent as obtained for the 300 μM C_{60} solutions in decalin-acetonitrile solvent mixtures. Sudden change in the scattered light intensity above $\varepsilon \sim 12.5$ clearly indicates the aggregation of C_{60} in the solution.

Below this critical polarity C_{60} remains as monomer and above this critical polarity it forms aggregates in solution. This critical polarity in terms of the dielectric constant (ε) of the solvents is found to be $\sim 13 \pm 1$. Figure 3 shows the changes in the absorbances vs. the solvent polarity (ε) for C_{60} solution in different solvent mixtures. Figure 4 shows a similar plot for the scattered light intensity in DLS studies vs. the dielectric constant of decalin-acetonitrile solvent mixtures indicating the onset of aggregation at $\varepsilon \sim 12.5$. All these experiments show that the solvent polarity is a critical parameter in governing the formation of the C_{60} aggregates.

The photoluminescence (PL) spectra of the fullerene aggregates have been compared with those of the crystalline materials [40]. The PL spectra of solutions containing the aggregates differ substantially from the unassociated fullerenes. The main effect of the aggregation is the appearance of the excimer like features in the PL spectra. Ahn *et al.* [40] have reported that the PL spectra of C_{60} aggregates in concentrated toluene solutions (0.7–3.0 mM) resembles that of crystalline solid except that the line widths were broader and that the energy corresponding to the electronic emission in the aggregate is located between that of the crystal and the monomer. The observed blue shift of the spectrum relative to the crystal was attributed to the quantum confinement effects. Aggregates were ~ 2.4 nm in diameter corresponding to ~ 3 weakly bound C_{60} molecules. Aggregation of fullerene is also reported to occur in CS_2 solution [41]. Dimer formation is also reported in chlorobenzene solutions [42]. Fujitsuka *et al.* [43] have recorded the ground state absorption spectra of C_{60} aggregates in CS_2-ethanol mixtures. The absorption spectra of the aggregates are quite broad with a long absorption tail towards the red edge of the spectrum and the absorption peak is blue shifted as compared to the free C_{60} molecules in CS_2. They have also measured the particle of size ~ 270 nm by DLS. Bensasson *et al.*

has shown that C_{60} is incorporated in liposomes mainly as aggregates [29].

The solubility of C_{60} in different solvents has been found to follow an unusual temperature dependence. It is seen that the solubility of C_{60} first increases, reaches a maximum and then decreases as the temperature is increased from 270 to 330 K. A theoretical model correlating the solubility of C_{60} with its aggregation in solution has been proposed by Bezmelnitsyn *et al.* [44,45] and the calculated results match well with the experiments.

On photoexcitation, C_{60} in DL, TL, BZ undergoes fast ISC process and the triplet quantum yield (Φ_T) is almost unity. In BZN, BZA and several other solvent mixtures, it is seen that the Φ_T value depends either on the C_{60} concentration or on polarity of the medium. For example, dilute solutions (<200 μM) of C_{60} in BZA shows the Φ_T value almost close to unity, where as beyond $\sim 200 \mu$M concentration, where C_{60} undergoes aggregation in BZA solution, the Φ_T reduces gradually with an increase in the C_{60} concentration (see Figure 5A). Similar results are also seen for the C_{60} aggregates in BZN solutions, where Φ_T is seen to decrease with the C_{60} concentration above $\sim 100 \mu$M solution and reduces only to ~ 0.32 at $\sim 350 \mu$M of C_{60}. On contrary, the Φ_T values in BZ, DL and TL is always found to be close to unity, irrespective of the C_{60} concentrations used (cf. Figure 5). These results in BZ, DL and TL clearly
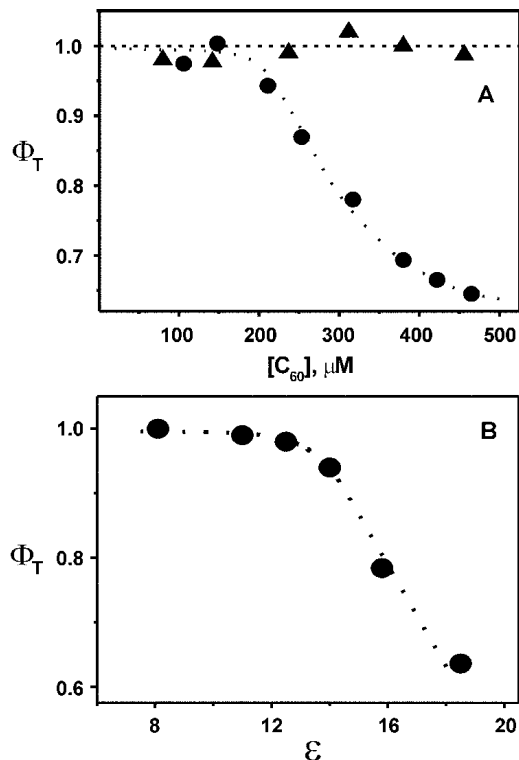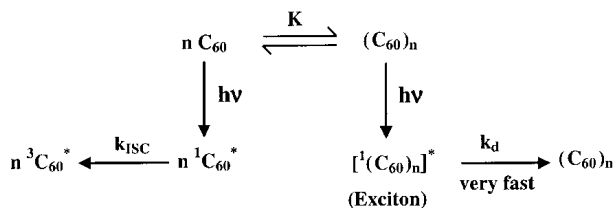

Figure 5. (A) Plot of the triplet quantum yields (Φ_T) versus the concentration of C_{60} in benzonitrile solution ($\bullet$) and in decalin ($\blacktriangle$). (B) The plot of Φ_T versus the dielectric constant (ε) of the solvents for C_{60} solutions in decalin-acetone solvent mixtures.

$$n\,C_{60} \underset{}{\overset{K}{\rightleftharpoons}} (C_{60})_n$$

Scheme 1.

demonstrate the absence of any aggregation process in these solvents even at very high C_{60} concentrations.

Similar to neat organic solvents, Φ_T for C_{60} in different solvent mixtures is seen to vary with the polarity of the medium. Figure 5B shows the variation of the Φ_T for C_{60} solutions in DL-acetone solvent mixtures. It is evident from this figure that the value of Φ_T is close to unity as long as dielectric constant of the medium is less than the critical value ($\varepsilon \sim 13 \pm 1$). Where as for the medium with polarity beyond this critical value, Φ_T gradually decreases with the solvent polarity.

The decrease in the Φ_T for C_{60} with the extent of aggregation process is attributed to the low ISC efficiency and the fast dissipation of the excitation energy in the aggregates. This is depicted in Scheme 1. Nakamura et al. [46] have shown that in solid state the excited singlet state of C_{60} decays in <1 ps. This fast relaxation is attributed to the formation of charge-transfer (CT) complexes following the excitation process, which decay to the ground state via non-radiative charge-recombination (CR) processes. The presence of two types of relaxations in the aggregates, one fast <2 ps and the other slower (>100 ps), have also been confirmed by our results using femtosecond laser flash photolysis experiments [47].

Effect of solvent polarity on the aggregation can be understood from the following considerations. Solubilization of C_{60} in a solvent is essentially due to an interplay between following three dispersive interactions, namely, (i) solvent-solvent ii) solute-solvent and iii) solute-solute interactions. C_{60} creates a large hole in the solvent structure upon its dissolution and thus disturbs the solvent-solvent interactions (i) to a large extent. Since interaction (ii) is reasonably weak as it is of van der Wall's type, it does not compensate for the disturbance in the interactions of type (i) in high polarity solvents. Under such conditions type (iii) interaction will be preferred resulting in the aggregation of C_{60} in solution. Our results indicate that such a situation arises when ε of the medium exceeds ~13, when the C_{60} molecules prefer to undergo aggregation. Solubility of fullerene in the medium is also found to be another important parameter that controls the aggregation process. Thus, even in higher polarity solvent, if the solubility is less than the critical concentration required, the fullerene aggregation is not observed in that solvent.

Apparently there seems to be some kind of anomaly in the aggregation behavior of C_{60} in nonpolar solvents like benzene and toluene, where the solubility of C_{60} is higher than those in

mixed solvents described above. The theoretical treatment of Bezmelnitsyn [44,45] on the unusual temperature dependence of the C_{60} solubility in different solvents is also based on the aggregation of the fullerene in the solution. In our opinion, the aggregation numbers and sizes of the aggregates in neat solvents like benzene and toluene are small. For example, in benzene we could not detect any particles >6 nm by DLS measurements. On the contrary, in mixed solvents and neat polar liquids like benzonitrile where solubility of C_{60} is limited, the aggregates are large with sizes >100 nm [32]. In fact, our results in nonpolar solvents like BZ, TL, etc., indicate the existence of C_{60} in its monomeric form rather than in the aggregated form, as indicated by Ying et al. [37] and Rudalvige et al. [39].

Unlike C_{60}, C_{70} does not form aggregates in polar solvent BZN. Detailed spectroscopic studies of C_{70} solutions in different mixed solvents show that, like C_{60} a critical solvent polarity is also required for the aggregation of C_{70}. This critical polarity is, however, found to be quite higher, 29 ± 2 [36], much higher than the critical solvent polarity required for C_{60} ($\varepsilon \sim 13 \pm 1$). Changes in the absorption characteristics with the solvent composition for C_{70} solution in different solvent mixtures are shown in Figure 6. Much higher critical solvent polarity
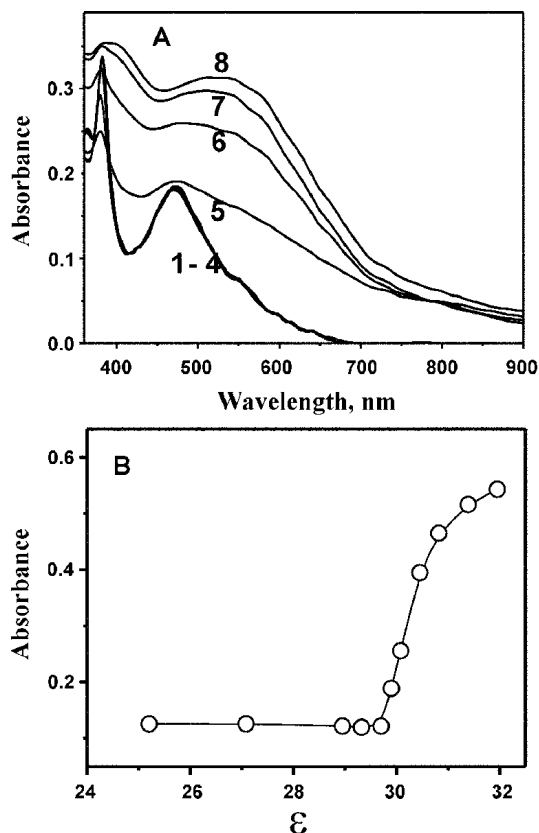

Figure 6. (A) Absorption spectra of C_{70} solution in benzene-acetonitrile solvent mixtures at different solvent compositions: (1) 0, (2) 30, (3) 50, (4) 65, (5) 70, (6) 72, (7) 75 and (8) 85% of AN in BZ. (B) Plot of absorbance at 550 nm versus ε for C_{70} solutions in benzonitrile-methanol.

required for C_{70} aggregation as compared to that of C_{60} has been explained on the basis of the higher polarizability of the former molecules compared to that of the latter [36].

Besides fullerenes, C_{60} and C_{70}, it is found that several fullerene derivatives also form aggregates in solutions [48-53]. Functionalization of fullerenes with hydrophilic groups promotes the water solubility of the fullerenes and at the same time leads to the irreversible formation of aggregates. For example Guldi *et al.* have shown that several C_{60} derivatives like, $C_{60}C(COOH)_2$, $C_{60}(C_9H_{11}O_2)(COOH)$, etc. form aggregates with the hydrophobic C_{60} core in the centre and the hydrophilic carboxylic groups sticking into the water phase [48]. The forces involved in the aggregation of the fullerene derivatives have been reported to be very strong and irreversible [49]. However, it is reported that the cluster formation by the fullerene derivatives can be prevented upon embedding the single fullerene molecules into the cavity of γ-cyclodextrin [54-57].

Photoinduced charge separation, charge recombination and electron transfer reactions of fullerenes

Fullerenes, C_{60} and C_{70}, have high electron affinities and thus readily accept an electron from an electron donor to form its anions radical [58]. Fullerenes also display interesting charge-transfer (CT) and electron transfer (ET) chemistry, both in their ground and excited states. The reduction potentials of C_{60} and C_{70} are reported to be very similar (–0.33 V vs Ag/AgCl in BZN solutions for both C_{60} and C_{70} [59]). Thus both C_{60} and C_{70} show quite similar CT and ET characteristics with variety of electron donors.

Fullerenes in their ground states are reported to form CT complexes with variety of electron donors like, aliphatic and aromatic amines [60-66], phenothiazines [67], porphyrins [68], olefins [69,70], tetrathiafulvene [71], etc. [72-74]. Many of these complexes are reported to display interesting properties like, ferromagnetism (e.g. C_{60}-tetrakis(dimethylamino)ethylene complex [58,75]) and non linear optical behaviors (e.g. C_{60}-N,N-diethyl aniline complex [61]). Among different fullerene-electron donor systems, the interactions between fullerenes and different amine donors have been extensively investigated by a large number of research groups including ours [62-67]. The absorption spectra of fullerenes in solutions undergo significant changes on the addition of the amines due to the formation of CT complex between fullerene and amine molecules. The formation constants of fullerene-amine CT complexes are, however, found to be quite low, only in the range of 0.1–10 $dm^3\ mol^{-1}$, indicating that the CT interactions in these ground state complexes are very weak. Formation of similar CT complexes by C_{60} and C_{70} with other electron donors like, polynuclear hydrocarbons, methylated benzenes, pyridine, etc. has recently been reported [76-78]. Weak ground state complex formation of C_{60} and C_{70} with aromatic solvent molecules via π–π interactions has also been reported from our group [62,63], and is supported by others [79,80]. It is

also demonstrated that the ground state π–π interaction between the fullerenes and the aromatic solvent molecules has a significant consequence in relation to the dissolution of the fullerenes in these solvents and also on the excited state interactions of the fullerenes with different electron donors.

Interactions of fullerenes in their excited states with different aliphatic and aromatic amine donors have been the subject of extensive studies in many research groups in the last decade [61-66]. The most interesting observation in relation to the photoinduced interactions of fullerenes with aromatic amines {e.g. N,N-dimethyl aniline (DMAN) and N,N-diethyl aniline (DEAN)} is the amine concentration dependent changes in the photoinduced processes [66]. Thus, depending on the concentrations of the amines used, two interesting situations have been encountered. At high amine concentrations (> ~1.5 $mol\ dm^{-3}$), where the ground state CT complex formation is dominant, the photoexcitation at the longer wavelength absorption band mainly causes the excitation of the fullerene-amine CT complex. The transient absorption studies show that the photoexcitation of the CT complexes causes an instantaneous charge separation (CS) to produce the radical ion-pair (RIP) states. At the lower concentration of the amines (< ~0.15 $mol\ dm^{-3}$), however, the photoexcitation initially produces the excited singlet (S_1) states of the fullerenes, which in turn undergo an CT/ET type of interactions, mostly via the formation of exciplexes [66]. For the fullerene-DMAN/DEAN systems interestingly it has been observed that both the excited CT complexes and the exciplexes give their characteristic and independent emissions. Typical exciplex and the CT emission spectra obtained in the C_{60}-DEAN system in decalin solution with lower (~0.16 $mol\ dm^{-3}$) and higher (~1.5 $mol\ dm^{-3}$) DEAN concentrations respectively are shown in Figure 7, along with the emission spectrum of C_{60} in the absence of any amine. Although the emission spectrum of only C_{60} shows clear vibronic structure, the emission spectra for the exciplexes and excited CT complexes are very broad and structureless.
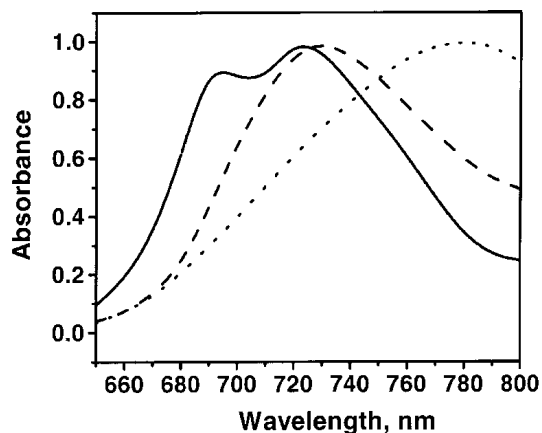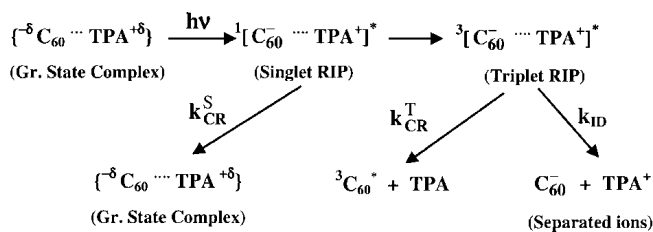

Figure 7. Fluorescence spectra of C_{60} (——), C_{60}-DEAN exciplex (- - -) and C_{60}-DEAN charge transfer complex (· · · ·) in decalin solution.

It has been observed that in C_{60}-DMAN/DEAN systems both the exciplex and the CT emissions are strongly dependent on the solvent polarities. Thus, on increasing the solvent polarity the intensities for both the emissions are seen to decrease drastically. From the polarity dependent spectral shifts for the exciplex and CT emissions the dipole moment of the exciplexes and the excited CT complexes for the C_{60}-DMAN/DEAN systems have been estimated to be in the range of (10-12) D and (25-27) D, respectively [66], indicating the highly polar nature of these species. A dipole moment value of about (25-27) D for the excited CT complexes further indicates that the photoexcitation of the ground state fullerene-amine CT complexes results in a complete charge transfer from the amine donors to the fullerene acceptors. A direct evidence for such complete charge separation (CS) following the photoexcitation of the similar fullerene-amine CT complexes, namely C_{60}-diphenylamine (DPA) and C_{60}-triphenylamine (TPA) complexes, has been earlier obtained using picosecond laser flash photolysis technique [64].

Observation of distinctly different emission spectra for the exciplexes and the excited CT complexes in the C_{60}-DMAN/DEAN systems is a very interesting and important observation. These results clearly indicate that the exciplexes and the excited CT complexes are the two distinctly different identities, a question often puzzles the photochemists while dealing with excited state interactions in different donor-acceptor systems. Observation of the emissions from the photoexcited CT complexes in C_{60}-DMAN/DEAN systems is also very interesting to note as the examples of emissions from excited donor-acceptor CT complexes are really very rare [66]. In fact, the C_{60}-DMAN/DEAN systems appear to be unique and uncommon displaying both exciplex and CT emissions together.

Since the ISC process is very efficient for the excited singlet (S_1) state of the fullerene molecules, in most of the fullerene-electron donor systems with low donor concentrations, a good fraction of the fullerene S_1 states undergo ISC process to produce their triplet states (T_1). The T_1 states of the fullerenes thus formed can subsequently undergo either ET or energy transfer reactions with the donor molecules present in the solution, depending on the relative feasibility or ease of the two processes. Ito and coworkers have clearly demonstrated such competitive ET and energy transfer processes in different fullerene-electron donor systems by suitably designed experiments [70,72,81]. The different photoinduced processes occurring in the fullerene-electron donor systems can conceptually be presented as in Scheme 2. In this scheme, different abbreviations used are: F for fullerenes, D for donors, $^1F^*$, $^3F^*$ and $^3D^*$ for the S_1 and T_1 states of F and the T_1 state of D respectively, $h\nu_{CT}$ and $h\nu_{EXC}$ for the emissions from excited CT complexes and exciplexes respectively. The rate constants for the processes like ion dissociation, CT emission, exciplex emission, ISC and CS are represented by symbols like k_{ID}, k_{CT}, k_{EXC}, k_{ISC} and k_{CS} respectively.

As already mentioned, the photoexcitation of the fullerene-

High Donor Concentrations :

$$F + D \; \rightleftharpoons \; \{^{-\delta}F \cdots D^{+\delta}\} \xrightarrow{h\nu} \{F^- \cdots D^+\}^*$$

(Gr. State Complex)   (Excited CT Complex/RIP)

k_{CT} k_{ID}

$$\{^{-\delta}F \cdots D^{+\delta}\} + h\nu_{CT} \qquad F^- + D^+$$

(Gr. State Complex)   (Separated Ions)

Low Donor Concentrations :

$$F + D \xrightarrow{h\nu} {}^1F^* + D \longrightarrow \{^{-\delta}F \cdots D^{+\delta}\}^*$$

(Exciplex)

k_{ISC} k_{EXC} k_{CS}

$${}^3F^* + D \qquad F + D + h\nu_{EXC} \qquad \{F^- \cdots D^+\}$$

(RIP)

(Electron Transfer) $F^- + D^+$

(SSIP)

(Energy Transfer) $F + {}^3D^*$

Scheme 2.

amine ground state complexes results in the instantaneous CS in these systems to produce the RIP states. The charge recombination (CR) reactions in the RIP states in different fullerene-amine systems have also been the subject of extensive investigation. The fullerene-amine systems like, C_{60}-diphenyl amine (DPA) and C_{60}-triphenyl amine (TPA) systems, has been investigated quite extensively in our laboratory [64] and are found to display many interesting features. Thus, in the C_{60}-TPA system, it has been observed that the CR reaction in the RIP results in the quite efficient formation of the C_{60} triplet state. In nonpolar solvent like benzene, the C_{60} triplet yield (Φ_T) following CR reaction in the RIP state in C_{60}-TPA system has found to be as high as about 0.9. It is, however, seen that the Φ_T values in the C_{60}-TPA system gradually reduces with an increase in the solvent polarity. The lifetime of the RIP state (τ_{RIP}) in C_{60}-TPA system is also seen to drastically reduces with an increase in the solvent polarity. Correlating the Φ_T and τ_{RIP} in different solvents of varying polarity Scheme 3 has been proposed for the C_{60}-TPA system. The reduction in the Φ_T and τ_{RIP} values with solvent polarity has been understood to be due to the enhancement in the ion-dissociation (ID) rate (k_{ID}) with an increase in the solvent polarity. Similar to C_{60}-TPA system, the effect of solvent polarity on the rate of CR and back electron transfer (BET) reactions has also been investigated for C_{60}-phenothiazines systems [67].

Unlike C_{60}-TPA system, the C_{60} triplet yield following CR reaction in the RIP state in C_{60}-DPA system is found to be substantially low, even in the nonpolar solvents. Thus the Φ_T

$$\{^{-\delta}C_{60} \cdots TPA^{+\delta}\} \xrightarrow{\text{h}\nu} {}^1[C_{60}^- \cdots TPA^+]^* \longrightarrow {}^3[C_{60}^- \cdots TPA^+]^*$$

(Gr. State Complex)   (Singlet RIP)   (Triplet RIP)

$$k_{CR}^S \qquad\qquad k_{CR}^T \qquad\qquad k_{ID}$$

$$\{^{-\delta}C_{60} \cdots TPA^{+\delta}\} \qquad {}^3C_{60}^* + TPA \qquad C_{60}^- + TPA^+$$

(Gr. State Complex)   (Separated ions)

Scheme 3.

value for C_{60}-DPA system in benzene solution is found to be only about 0.23 in comparison to the Φ_T value of about 0.9 for C_{60}-TPA system in the same solvent. Further, the τ_{RIP} values for the C_{60}-DPA system are always found to be much lower (e.g. $\tau_{RIP}\sim240$ ps for C_{60}-DPA system in benzene) than those for the C_{60}-TPA system (e.g. $\tau_{RIP}\sim1300$ ps for C_{60}-DPA system in benzene). Thus C_{60}-DPA system appears to behave differently than the C_{60}-TPA system under similar conditions and the differences has been explained on the basis of the structural difference between DPA and TPA molecules. Structurally DPA and TPA differ with respect to the presence and absence of the amino hydrogen (NH group). Since in the radical cationic state the NH hydrogen in DPA is expected to become quite acidic, it is proposed that there is a proton transfer channel involved along with the other channels to decay the RIP state in C_{60}-DPA system. Involvement of the proton transfer process in the RIP state of the C_{60}-DPA system has been confirmed by using deuterated DPA as the donor, whereby both Φ_T and τ_{RIP} values are seen to increase substantially (about 0.38 and 390 ps respectively) in comparison to the Φ_T and τ_{RIP} values (0.23 and 240 ps respectively) for undeuterated C_{60}-DPA system. Effect of proton transfer process on the C_{60} triplet yield has also been observed for C_{60}-phenothiazine systems [67].

The CS and CR reactions have also been investigated in many other fullerene-electron donor systems using donors like, different aliphatic and aromatic amines, phenothiazines, different olifines etc. [62-67]. In the C_{60}-triethylamine (TEA) system, though there is no NH hydrogen in TEA, yet a proton transfer process has been indicated [64]. It is proposed that the α-hydrogen atom of one of the alkyl group of the TEA cation radical act as a source of the acidic proton (cf. Scheme 4). In the C_{60}-TEA system the τ_{RIP} value is found to be only about 200 ps in benzene solution.
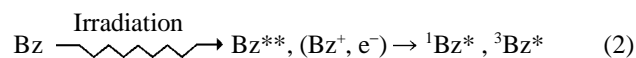
The triplet state of C_{60} is also a powerful electron acceptor, with a reduction potential of ~1.14 V (vs. SCE in acetonitrile solution [14]) and is known to accept electrons from several electron donors to give the donor cation radicals and the $C_{60}^{\bullet-}$ anion radical. Electron transfer reactions from many electron
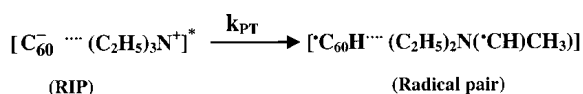
donors like carbazole, polyvinyl carbazole, nicotinamide derivatives, olifines, etc. to ${}^3C_{60}^*$ have been reported in the literature [82-86]. In some of these fullerene-electron donor systems, occurrence of processes like Diels-Alder reactions has been reported, resulting in the formation of synthetically important fullerene derivatives [5,87,88]. Among different systems photocycloaddition of enes to C_{60} by Diels-Alder reactions has been investigated extensively and found to be quite successful from the synthetic point of view. Zhang et al. [89] have reported the cycloaddition of ynamines to the triplet state of C_{60} and is proposed to occur via CT mechanism. Mikami et al. [90,91] has reported that the Diels-Alder cycloaddition reactions between ${}^3C_{60}^*$ and Danishefsky's dienes occur by step-wise bond formation processes via the photoinduced ET reaction. The $C_{60}^{\bullet-}$ anion radical has also been identified in the C_{60}-Danishefsky's diene systems by Mikami et al. [90,91]. In one of our recent studies on the photoinduced CT interactions between C_{60} and diphenylpolyenes (e.g. 1,4-dibutlybutadiene, DPB and 1,6-diphenyl-1,3,5-hexatriene, DPH) it has been found that one of the channel in which C_{60} triplet reacts with DPB and DPH is the formation of [2+2] cycloadduct [92]. In the C_{60}-DPB/DPH systems the CT interaction is seen to result in the formation of the ground state CT complexes, which on photoexcitation results in the formation of the RIP states. Detailed kinetic studies have also been made to resolve the different decay channels for the RIP states in C_{60}-DPB/DPH systems [92].

In one of the recent work from our laboratory on the interaction of C_{60} with a triphenylmethane dye, crystal violet (CV$^+$), a number of interesting observations have been made [93]. In this work the interaction of the triplet state of CV$^+$ with C_{60} has been investigated using pulse radiolysis technique. Following an electron pulse in benzene (BZ) solutions containing CV$^+$, the triple state of the dye (^{3}CV^{+*}) is produced by the following sequence of reactions [93].

$$Bz \xrightarrow{\text{Irradiation}} Bz^{**}, (Bz^+, e^-) \rightarrow {}^1Bz^* , {}^3Bz^* \qquad (2)$$

$$^1Bz^{**} \rightarrow {}^3Bz^* \qquad (3)$$

$$^3Bz^* + CV^+ \rightarrow Bz + {}^3CV^{+*} \qquad (4)$$

Since ^{3}Bz* has a higher energy (E$_T$~82 kcal/mol) than that of ^{3}CV^{+*}, triplet-triplet energy transfer process to CV$^+$ is very facile. Using this approach, ^{3}CV^{+*} has been generated and its properties have been characterized. Cascade energy transfer processes have also been used to obtain better yields for ^{3}CV^{+*} and also to confirm the results, using biphenyl (Bip) as the triplet sensitizer [94].

$$^3Bz^* + Bip \rightarrow {}^3Bip^* + Bz \qquad (5)$$

$$^3Bip^* + CV^+ \rightarrow {}^3CV^{+*} + Bip \qquad (6)$$

Figure 8 shows transient absorption spectra of the species produced on energy transfer from ^{3}Bz* to CV$^+$ (at 1 μs) giving

$$[C_{60}^- \cdots (C_2H_5)_3N^+]^* \xrightarrow{k_{PT}} [{}^\bullet C_{60}H \cdots (C_2H_5)_2N({}^\bullet CH)CH_3)]$$

(RIP)   (Radical pair)

Scheme 4.
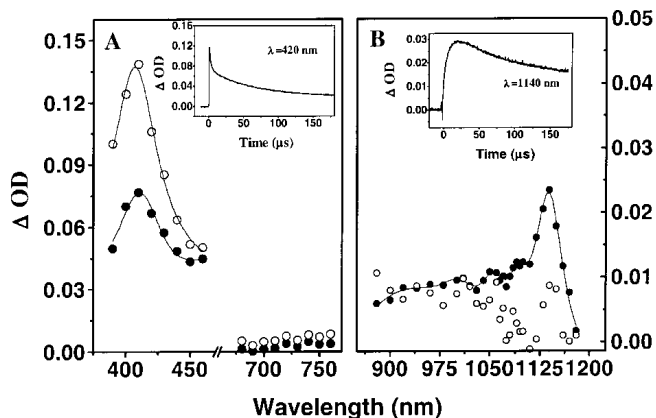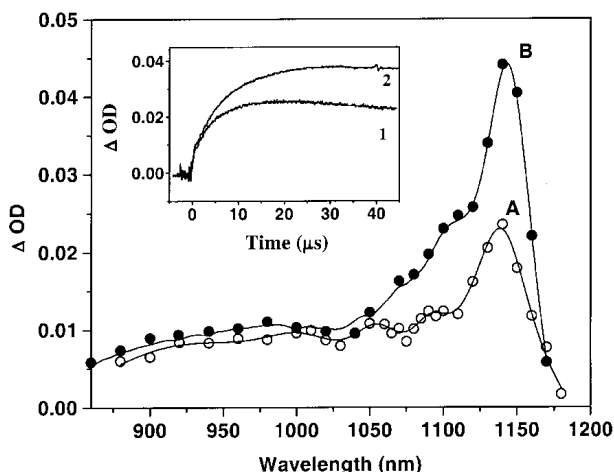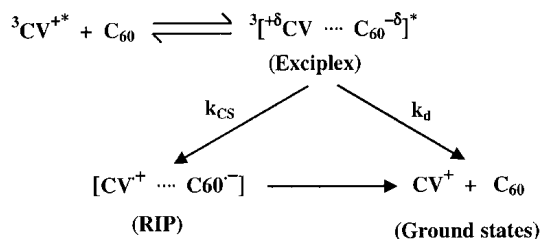
Figure 8. Transient absorption spectra recorded in N_2 saturated benzene-acetonitrile (15%) solutions containing 1) 1.6×10^{-3} mol dm^{-3} CV$^+$ and 100×10^{-6} mol dm^{-3} C_{60} at 1 μS ($\bigcirc$) and 2) at 10 μS ($\bullet$) in the spectral region of (A) 380–750 nm and (B) 880–1220 nm. Inset of A shows the decay of absorption at 420 nm and that of B shows the growth and decay of absorption at 1140 nm.

^{3}CV$^+$* with maximum at 420 nm, and the reaction of ^{3}CV$^+$* with C_{60} (at 10 μs) to give an absorption band at around 1140 nm. The inset of Figure 8 also shows the decay of the ^{3}CV$^+$* at 420 nm and that of the transient with peak at ~1140 nm. The initial fast decay at 420 nm shows the decay of the ^{3}CV$^+$* and the slow decay corresponds to unreacted ^{3}CV$^+$* and some absorption due to species produced on reaction of ^{3}CV$^+$* with C_{60}. No triplet of C_{60} (λ_{max} ~ 740 nm) could be seen indicating that the energy transfer from ^{3}CV$^+$* to C_{60} does not take place. Figure 9 shows the increase in the absorption in the near IR region (at 10 μs) in the absence and presence of the triplet sensitizer Bip. The inset of the Figure 9 shows the rise of the

absorption in both the solutions, respectively. The absorption due to ^{3}CV$^+$* at 420 nm gets reduced as C_{60} concentration is increased and correspondingly that at 1140 nm gradually increases. No absorption due to the $C_{60}^{\bullet-}$ at 1070 nm [95] was seen. The new absorption band with maxima at ~1140 nm is assigned to the exciplex formation by the interaction of the ^{3}CV$^+$* with the ground state of C_{60}. Since the lifetime of the 1140 nm transient is very long (>10 μs), it is proposed that the ^{3}CV$^+$*–C_{60} exciplex is having a spin multiplicity of three (i.e. triplet). On changing the polarity of the medium, the 1140 nm peak is seen not to undergo any significant shift. The absorbance in the 1140 nm peak is, however, seen to decrease gradually with an increase in the solvent polarity. Even in the highest polarity solvent used in this study there is no appearance of an absorption peak corresponding to the $C_{60}^{\bullet-}$ at 1070 nm. Thus, it is indicated that the ^{3}CV$^+$*–C_{60} exciplex even might be converting to the radical ion-pair (RIP) state on increasing the solvent polarity, but the RIP does not dissociate to give the solvent separated ion-pair (SSIP). The results indicate that both ^{3}CV$^+$*–C_{60} exciplex and RIP mostly decay back to the ground state reactants. It might be possible that the solvent polarity region covered in this study is not sufficient enough to produce the SSIP in the present system. To rationalize the observed results in the CV$^+$-C_{60} system, Scheme 5 has been proposed.

Interestingly, it has been seen that the interaction of the triplet state of C_{60} (^{3}C$^*_{60}$) with CV$^+$ does not show the transient absorption with peak at 1140, indicating that ^{3}C$^*_{60}$ does not form exciplex with the ground state of CV$^+$ [93]. Relative triplet state energies (E_T) of CV$^+$ and C_{60} could be responsible for this observation. Since E_T for CV$^+$ is higher than that of C_{60}, ^{3}CV$^+$* can form exciplexes interacting with the ground state of CV$^+$. With much lower E_T, the interaction of ^{3}C$^*_{60}$ with the ground state of CV$^+$ to form exciplex seems to be energetically unfavorable.

In the ET reactions using C_{60} as the acceptor, the reorganizational energy associated with the ET processes is unusually small. Under such situation, the ET reactions for many of C_{60}-electron donor systems appears in the Marcus inverted region, causing the back electron transfer (BET) processes often very minimum [96]. Composites of several donor-acceptor pairs have been investigated using C_{60} with many conjugated, polymeric and semiconductor systems that act as efficient electron donors [96]. In mixed composites

Figure 9. Transient absorption spectra recorded in N_2 saturated benzene-acetonitrile (15%) solutions containing (A) 1.6×10^{-3} mol dm^{-3} CV$^+$ and 100×10^{-6} mol dm^{-3} of C_{60} and (B) 20×10^{-3} mol dm^{-3} Biphenyl, 1×10^{-3} mol dm^{-3} CV$^+$ and 50×10^{-6} mol dm^{-3} C_{60}. The absorption values are taken at the maximum growth (10 μs). Inset: Kinetic traces recorded at 1140 nm in the above solutions: A (1) and solution B (2).
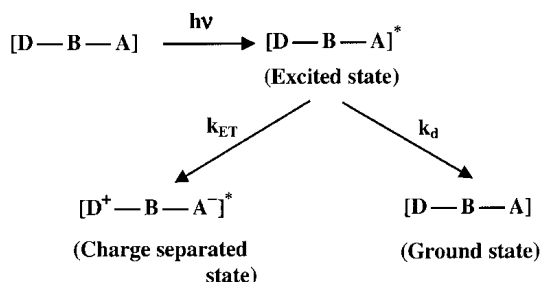

Scheme 5.

containing donor-acceptor pairs, ultrafast photoinduced ET is seen to occur with high quantum yield. This feature attracted interdisciplinary efforts to utilize conjugated polymer-C_{60} blends as novel materials for photovoltaic cells to convert photons into electrons. Tendency of C_{60} to phase separate out and crystallize, limits its solubility in conjugated polymers. However, uniformity and high quality of such systems are essential requirements for opto-electronic device applications. Hence soluble functionalized derivatives of fullerenes are being synthesized to suppress the phase separation when used in polymer blends.

To obtain better efficiency for the ET process, rather than depending on intermolecular ET, intramolecular approaches using synthetic diads and triads containing C_{60} acceptor and various donors have been followed [97-101]. Photosynthetic systems are complex in nature and attempts have been made to design model molecular systems that can mimic various primary processes in natural photosynthesis. A simplest model is a dyad molecule in which a donor group (D) is covalently linked to an acceptor group (A) through a flexible bridging unit (B) i.e. D-B-A. Photoexcitation of either D or A leads to the ET from D to A and results in the generation of the cation radical of D and anion radical of A in a dyad molecule (see Scheme 6).

Stabilization of the charge-separated state by avoiding BET is a very important aspect for the success of such molecular systems for energy conversion devices. Efforts are being made to study the rate of ET processes by tuning the energetics of the D-A pair and optimizing the distance between the D and A in the molecule by suitable spacers (B). Excellent acceptor properties of C_{60} make it an ideal candidate to design artificial photosynthetic systems. C_{60} based dyads with donors like porphyrins, phthalocyanines, ruthenium complexes, ferrocenes, and amines have been synthesized. Formation of $C_{60}^{\bullet-}$ and $D^{\bullet+}$ radicals serves as monitor for the charge separation in these dyads. Fulleropyrrolidine derivative bearing an oligo phenylenevinylene substitutent has been proposed as a suitable candidate for constructing a solar energy conversion system [102-104].

The remarkable electron accepting properties of fullerenes evoked the implementation of fullerenes as an electron acceptor unit in the design of novel artificial light harvesting superstructures [105-107]. The ultimate aim of such design is to convert sunlight into a usable form of energy with near unit quantum efficiency. One viable approach to the photosynthetic modeling has been the covalently linking various redox active chromophores to give a single supermolecular structure that will govern the unidirectional flow of electron following photoexcitation. In this context, light induced intramolecular charge separation has been reported for various C_{60}-based donor-acceptor systems endowed with various electron donors. The key to accomplish this is to optimize the CS states. Two important concepts have emerged: (1) to increase the D-A separation distance and (2) the use of multi-component systems e.g. D-A dyads, triads, tetrads in the supermolecular structures. The important task in this game is to design a well-defined redox gradient along the multiple redox centers that can give a unidirectional flow of electrons through a long electron donor-acceptor chain over a long distance [103]. In near future such a goal seems to be achieveable.

CONCLUSIONS

Due to the exotic structures and the remarkable electron accepting properties, the fullerenes display interesting solvatochromism, aggregation behavior and the charge transfer and the electron transfer characteristics. In the present article we have summarized the research work carried out in our laboratory on the solvatochromism, aggregation behavior and charge transfer and electron transfer interactions of fullerenes, C_{60} and C_{70}, along with the relevant results from other laboratories. It has been understood that the unusual solvatochromism of C_{60} and C_{70} is largely associated with the aggregation of these molecules in solution. It has been established that the solvent polarity plays a significant role in the aggregation process of the fullerenes in solution. Thus, the fullerene aggregation in solution occurs only when the solvent polarity exceeds a critical value required for such process. The critical solvent polarity required for C_{70} aggregation is found to be much higher than that required for C_{60} aggregation, and is rationalized on the basis of the differences in the polarizability of the C_{60} and C_{70} molecules. Electron transfer and charge transfer interactions of fullerenes with different electron donors demonstrated many interesting and unusual observations. The observation of both exciplex and charge transfer emissions in the C_{60}-aromatic amine systems are unique examples to demonstrate that the exciplexes and the excited charge transfer complexes are two distinctly different species. The fullerene-aromatic amine systems have also been found to be the interesting systems to display the charge separation and charge recombination processes and thus possess tremendous academic and application oriented interests. Development of the supramolecular framework involving fullerenes as the efficient electron acceptors along with suitable other redox centers having well-defined redox gradient for unidirectional flow of electron following photoexcitation seems to be a viable approach to design an efficient

$$[D\!-\!B\!-\!A] \xrightarrow{\;h\nu\;} [D\!-\!B\!-\!A]^*$$

(Excited state)

k_{ET} $\qquad$ k_d

$$[D^+\!-\!B\!-\!A^-]^* \qquad\qquad [D\!-\!B\!-\!A]$$

(Charge separated $\qquad\qquad$ **(Ground state)**
state)

Scheme 6.

light harvesting system.

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