J. Phys. Chem. A **1999,** *103,* 4993−5002

Interaction of Ground and Excited (S_1) States of C_{60} and C_{70} with Aromatic Amines: Exciplex and Charge-Transfer Emissions

M. C. Rath, H. Pal,* and T. Mukherjee

Radiation Chemistry and Chemical Dynamics Division, Bhabha Atomic Research Centre,
Trombay, Mumbai 400 085, India

Received: November 30, 1998; In Final Form: March 16, 1999

Emissions from both exciplexes and excited charge-transfer (CT) complexes have been observed for the fullerene−aromatic amine systems in nonaromatic solvents and solvent mixtures using steady-state fluorescence measurements. Support for the exciplex and CT emissions has also been obtained from the time-resolved fluorescence measurements. Both emissions are very sensitive to the polarity of the solvents. From the solvatochromic shifts of the emission maxima, dipole moments (μ) of the exciplexes and the excited CT complexes have been estimated. For C_{60}−*N*,*N*-dimethylaniline (DMAN) and C_{60}−*N*,*N*-diethylaniline (DEAN) systems, the μ values for the exciplexes and the excited CT complexes are in the ranges 10−12 and 25−27 D, respectively. Both species are thus very polar in nature. In aromatic solvents the fullerene−aromatic amine systems behave differently, without forming any exciplexes, though the fullerene emissions are quenched by the amines with almost diffusion-controlled rates. CT emissions are also not observed in the aromatic solvents. The π-electrons of the solvent molecules are supposed to be responsible for the unusual behavior of these solvents on the present systems.

1. Introduction

Unusual structure and reactivity of fullerenes, C_{60} and C_{70}, have attracted considerable attention in a variety of research areas.[1−15] Fullerenes have high electron affinities and thus readily form anions on electrochemical reduction.[4,16−20] Fullerenes also display interesting charge-transfer (CT) chemistry, both in their ground and excited states, with a number of aromatic amines.[1,2,21−24] The reduction potentials of C_{60} and C_{70} are reported to be very similar[25] (−0.33 V vs Ag/AgCl in benzonitrile for both C_{60} and C_{70}). Thus, they are expected to show similar electron-accepting characteristics with a variety of electron donors. The fullerene−amine complexes have been proposed to be CT in character. Picosecond laser flash photolysis of these complexes have demonstrated interesting charge-separation (CS) and charge-recombination (CR) reactions.[21,22]

During the past few years many interesting observations have been reported on the interaction of the excited (S_1) state of the fullerenes with the amine donors.[1,2,21−26] Wang[26] first observed that the S_1 state of C_{70} interacts with *N*,*N*-dimethylaniline (DMAN) to form an exciplex in a nonpolar solvent hexane (HX). In our earlier studies[23,24] we have demonstrated the formation of exciplexes by the S_1 states of both C_{60} and C_{70} with aromatic amines such as DMAN and *N*,*N*-diethylaniline (DEAN) in nonpolar nonaromatic solvents such as HX, cyclohexane (CHX), and methylcyclohexane (MCHX). Sun et al.[27,28] also reported similar observations for the fullerene−DMAN/DEAN systems in nonpolar nonaromatic solvents. One interesting observation in the case of the C_{60}−DMAN/DEAN systems in nonpolar nonaromatic solvents such as HX, CHX, and MCHX is that the overall fluorescence intensity initially increases substantially up to a certain amine concentration and then decreases as the amine concentration is made further higher.[23,24,27,28] Similar initial increase and then decrease of the fluorescence lifetime with increasing amine concentration have also been observed in the case of the C_{60}−DMAN/DEAN systems in nonpolar nonaromatic solvents.[23,24] These unusual observations of the C_{60}−aromatic amine systems in nonpolar nonaromatic solvents have not been properly explored either in our earlier work or in the work of Sun et al. In the present work we have investigated the exciplex formation by the excited (S_1) fullerenes C_{60} and C_{70} with DMAN and DEAN in different solvents and solvent mixtures in order to find an explanation for the unusual fluorescence behavior of the C_{60}−DMAN/DEAN systems.

In our earlier studies[23,24] as well as in those of Sun et al.[27,28] it has been observed that the aromatic solvents such as benzene (BZ) and toluene (TOL), which are otherwise considered to be nonpolar solvents, behave differently from the nonpolar nonaromatic solvents toward the fullerene−amine systems. There has been no evidence for exciplex formation for either of the fullerene−DMAN/DEAN systems in BZ and TOL, though the fluorescence of both C_{60} and C_{70} get quenched efficiently by the aromatic amines (quenching rate constants, $k_q \approx 2 \times 10^{10}$ $dm^3\ mol^{-1}\ s^{-1}$).[23,24] From the observed small differences in the absorption spectra of the fullerenes in aromatic and nonaromatic solvents, we have proposed the formation of ground-state complexes between the fullerenes and the aromatic solvent molecules. It has been proposed that the differences in the behavior of the fullerene−DMAN/DEAN systems in aromatic and nonaromatic solvents can be related to the formation of these complexes. Sun et al.,[27,28] however, have proposed a different view in relation to the behavior of the fullerene−amine systems in aromatic solvents. According to these authors, high polarizability of the aromatic solvents favors a direct electron transfer to form the ion-pair states rather than the formation of exciplexes as the intermediates. Using a series of solvent mixtures, Sun et al.[27] have also shown that the fullerene−amine exciplexes are very sensitive to the polarity and polarizability

---

* To whom correspondence should be addressed. Fax: (+)91-22-5505151.

10.1021/jp984550j CCC: $18.00

of the solvents. These authors, however, have not given any detailed analysis of their results. Our present investigation is aimed toward resolving the differences between the views of Sun et al.[27,28] and ours[23,24] in relation to the behavior of the fullerene−amine systems in aromatic and nonaromatic solvents and also toward finding the reason for the high sensitivity of these systems to the polarity and polarizability of the solvents.

2. Materials and Methods

Fullerenes C_{60} and C_{70} were obtained from SES Research, Inc. (purity of the samples is ≥99.8%). All solvents, except Decalin, were of spectroscopic grade from Spectrochem India. Decalin (DL) was of synthesis grade from E. Merck and purified by vacuum distillation. DMAN and DEAN were obtained from Fluka and purified by vacuum distillations just before use.

Ground-state absorption spectra of the fullerene solutions were recorded using a Shimadzu model 160A UV−vis spectrophotometer. Fluorescence spectra were recorded using a Hitachi model 4010 spectrofluorometer coupled with a Hamamatsu R928F photomultiplier tube in a right-angle geometry. The excitation and emission slits were kept at 5 nm and the excitation wavelength at 540 nm. Fluorescence spectra were recorded without applying any correction for the wavelength-dependent instrument response.

Fluorescence lifetime measurements were carried out at the Tata Institute of Fundamental Research, Mumbai, using a time-resolved fluorescence measurement setup. The instrument works on the principle of time-correlated single-photon-counting (TCSPC) technique. Briefly, the output of a picosecond (4 ps) titanium:saphire laser (Spectra Physics, Tsunami) at around 800 nm (average power of ∼1 W, frequency of ∼82 MHz) was passed through a pulse picker to reduce its frequency to about 800 kHz (with average power of about 15 mW). The 800 nm laser pulse was then used to generate the second harmonic at 400 nm with an average power of about 1 mW. The second harmonic light was used to excite the sample. A small part of the reflected 400 nm light was used to generate the start pulse for the TCSPC instrument. The fluorescence signal gave the stop pulse for the TCSPC. Observed fluorescence decays were analyzed by a reconvolution procedure using a proper instrument response function, obtained by substituting the sample cell with a light scatterer. All decay curves were fitted as a single-exponential function as

$$I(t) = B \exp(-t/\tau_f) \qquad (1)$$

where τ_f is the fluorescence lifetime of the sample and B is the pre-exponential factor.

3. Results and Discussion

3.1. Ground-State Interaction of the Fullerenes with Aromatic Amines. It is well-known that the absorption spectra of C_{60} and C_{70} undergo significant changes on addition of amines to the solutions.[1,2,21−24] These spectral changes have been attributed to the formation of the charge-transfer (CT) type of ground-state complexes between the fullerenes and the amines. In a nonpolar nonaromatic solvent like DL, both C_{60} and C_{70} form the ground-state complexes with DMAN and DEAN, as is evident from the changes in the absorption spectra of the fullerenes. Figure 1 shows some typical results for C_{60}−DEAN and C_{70}−DEAN systems in DL. In the present study the solvent DL is used as the reference nonpolar nonaromatic solvent because both C_{60} and C_{70} have reasonably high solubility in this solvent,[29] which makes it easier and less erroneous to investigate different aspects of C_{60} and C_{70} fluorescence in this solvent in comparison to other common nonpolar nonaromatic solvents such as HX, CHX, etc., where the solubility of the fullerenes is quite low.[29]

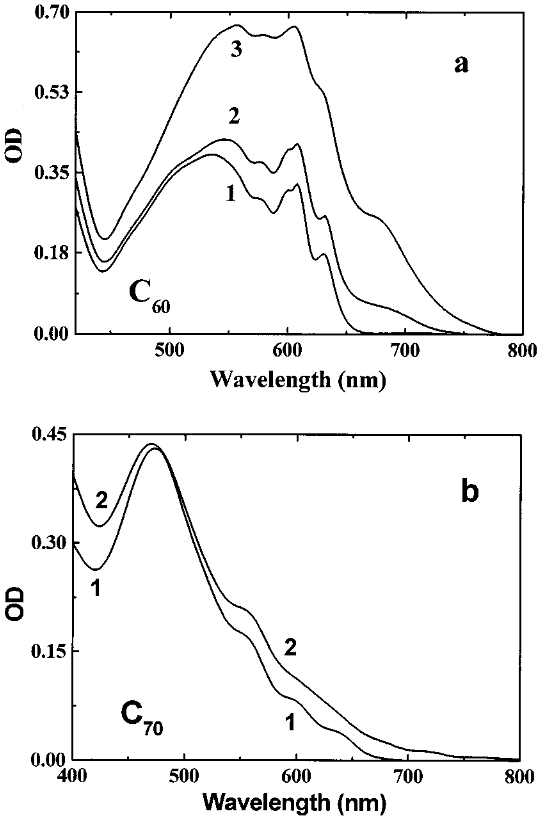


Figure 1. Ground-state absorption spectra of C_{60} and C_{70} in the presence of DEAN in Decalin: (a) C_{60} in the absence (1) and presence of (2) 0.16 and (3) 1.25 mol dm^{-3} of DEAN; (b) C_{70} in absence (1) and in the presence (2) of 1.25 mol dm^{-3} DEAN.

The equilibrium constant for the ground-state complex formation in the present systems can be estimated following the Benesi−Hildebrand relation[30] for a 1:1 complex formation (eq 2), modified for the cases having overlapping absorption for the fullerene and the complex.

$$\frac{1}{\Delta \mathrm{OD}(\lambda)} = \frac{1}{K C_A^0 \epsilon'(\lambda)}\left(\frac{1}{C_D}\right) + \frac{1}{C_A^0 \epsilon'(\lambda)} \qquad (2)$$

where $\Delta\mathrm{OD}(\lambda) = \{\mathrm{OD}(\lambda) - \mathrm{OD}_0(\lambda)\}$ and $\mathrm{OD}(\lambda)$ and $\mathrm{OD}_0(\lambda)$ are the observed optical densities at wavelength λ in the presence and the absence of the amines, respectively, C_D is the concentration of the donor (amine), C_A^0 is the total concentration of the acceptor (fullerene), K is the equilibrium constant for the fullerene−amine ground-state complex formation, $\epsilon'(\lambda) = \{\epsilon_{DA}(\lambda) - \epsilon_A(\lambda)\}$, and $\epsilon_{DA}(\lambda)$ and $\epsilon_A(\lambda)$ are the molar extinction coefficients of the donor−acceptor complex and free acceptor, respectively, at wavelength λ. The K values for the C_{60}−DMAN/DEAN systems in DL as estimated following eq 2 are listed in Table 1. For the C_{70}−DMAN/DEAN systems, as Figure 1 indicates, the changes in the absorption spectra are quite small, and we did not try to estimate K values for these systems. Wang,[26] however, estimated a complexation constant for the C_{70}−DEAN system as 0.4 dm^3 mol^{-1} in MCHX, which is almost in the similar range for the C_{60}−DMAN/DEAN systems. Thus, it is evident that the strength of interaction of C_{70} with the amines is very similar to that of C_{60}, though apparently, the

TABLE 1: Ground-State Complexation Constant (*K*) of C_{60} with DMAN and DEAN in Different Decalin−Acetone Mixed Solvents

	K	
solvents[a]	DMAN	DEAN
0% AC	0.19	0.78
1% AC	0.14	0.81
2% AC	0.22	0.96
3% AC	0.18	0.64
5% AC	0.25	0.61
10% AC	0.25	0.65

[a] Percentage of acetone (AC) by volume in Decalin.

spectral changes are much less prominent for the former in comparison to the latter systems. (cf. Figure 1).

To see the effect of solvent polarity on the ground-state complex formation, we determined *K* values for the C_{60}−DMAN/DEAN systems in a number of acetone (AC)−DL mixed solvent compositions. The AC composition was varied from 0 to about 10 vol %. The values of *K* thus obtained in the AC−DL mixed solvent systems are listed in Table 1. Up to about 10 vol % of AC in DL there is not much variation in the *K* values. Thus, it is evident that the solvent polarity does not have much effect on the ground-state fullerene−amine complex formation, and hence, the complexes are of very weak CT character. Another point to be noted from Table 1 is that the *K* values are always higher for DEAN than for DMAN, indicating stronger interaction of C_{60} with the former. This is an interesting observation because the oxidation potentials of DMAN and DEAN are very similar (+0.35 and +0.34 V vs Ag/Ag^+ in acetonitrile[31]). Thus, it is indicated that not only the redox characteristics but some other specific interaction may also play some role in determining the strength of interaction of the fullerene with the amines. The nature of the specific interaction, however, is not clear at this stage.

3.2. Excited-State (S_1) Interaction of the Fullerenes with Aromatic Amines. *3.2.1. C_{60}−DMAN/DEAN Systems.* The fluorescence spectra of C_{60} change significantly as DMAN/DEAN is added to the fullerene solution in DL. Thus, on addition of DMAN/DEAN to the C_{60} solutions, the initial fluorescence intensity substantially increases up to a certain concentration of the amines and then decreases as the amine concentration is further increased. It is also noted that when the amine concentration is increased, the vibrational structures of the C_{60} emission spectra in DL gradually becomes blurred and eventually disappears. The amine concentration at which the vibrational structures practically disappear is more or less similar to that at which the increase in the C_{60} fluorescence intensity reaches its maximum with the amine concentration. Another interesting point is that for the lower amine concentration region, where the fluorescence intensity gradually increases with the added amines, the observed fluorescence maxima do not change appreciably, though the fluorescence spectra become very broad and structureless. The fluorescence maxima for the C_{60}−DMAN/DEAN systems in DL appear around 720−726 nm for the amine concentration range of 0 to ~0.16 mol dm^{-3}. For the higher amine concentration region, where the C_{60} fluorescence intensity gradually decreases, the fluorescence maxima shift concomitantly to the longer wavelengths as the amine concentration is increased. For a change in the amine concentration from ~0.16 to ~1.25 mol dm^{-3}, the emission maxima shift from ~724 to ~780 nm. Typical results are shown in Figure 2 for the C_{60}−DEAN system in Decalin. Similar observations were also made in other nonpolar nonaromatic solvents such as HX, CHX, and MCHX.

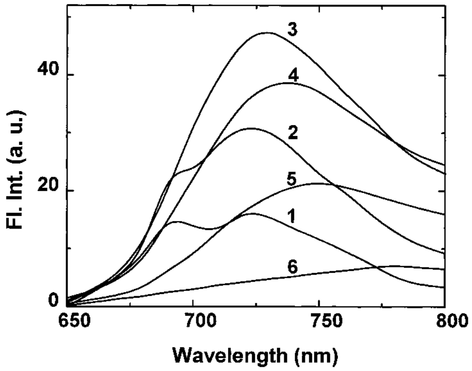


Figure 2. Fluorescence spectra of C_{60} in Decalin in the presence of different concentrations of DEAN. The amine concentrations are (1) 0.0, (2) 0.03, (3) 0.16, (4) 0.32, (5) 0.63, and (6) 1.25 mol dm^{-3}.

Low Amine Conditions. At the lower amine concentration regions (<0.16 mol dm^{-3}), where the changes in the ground-state absorption spectra of C_{60} are not very significant (cf. Figure 1), the gradual increase in the fluorescence intensity with the amine concentration and the concomitant disappearance of the vibrational structures in the fluorescence spectra indicate the formation of (C_{60}−DMAN/DEAN)* exciplexes. As indicated by the increase in the fluorescence intensity (Figure 2), it is evident that the efficiency of the exciplex emission is much higher than that of the C_{60} monomers. At an amine concentration of about 0.16 mol dm^{-3}, the observed fluorescence intensity for the C_{60}−DMAN/DEAN systems in DL and in other nonpolar nonaromatic solvents is about 2 times or more stronger than that of the initial C_{60} monomer emission. The emission spectra at this amine concentration can thus be considered to be predominantly due to the (C_{60}−DMAN/DEAN)* exciplex emissions with negligible contribution from the C_{60} monomer emission. The observed fluorescence peaks at the amine concentration of about 0.16 mol dm^{-3} were thus considered as the exciplex emission maxima for the present systems.

It is interesting at this point to consider the other possibilities for the increase in the C_{60} fluorescence intensity with the added amines. Since C_{60} is a very symmetric molecule (truncated icosahedral, point group I_h), the longest-wavelength transitions are highly forbidden.[32] Thus, the fluorescence quantum yield for C_{60} has been reported to be very low, viz. $\sim 2 \times 10^{-4}$ (Kim and Lee [33]) and $\sim 3.2 \times 10^{-4}$ (Ma and Sun [34]). It may be possible that in the presence of amine the order of symmetry in C_{60} is a bit reduced, and hence, the forbiddenness of the transition is slightly relaxed. It is then likely that an enhancement in the fluorescence yield of C_{60} may occur. That in the present case it is not simply due to this symmetry breaking is indicated from the fact that the increase in the fluorescence intensity is not continuous. It increases only up to a small concentration of DMAN/DEAN and then decreases as the amine concentration is further increased. If it was due to just the lifting of the symmetry restriction, then the fluorescence intensity should continuously increase with amine concentration or at the most it could reach some saturation value. Further, if it was the case of lifting the symmetry restrictions then it was expected that the rate of the radiative transition (k_f) for the excited (S_1) C_{60} should increase in the presence of amines. Since the observed fluorescence lifetime is defined as

$$\tau_f = 1/(k_f + k_{nr}) \tag{3}$$

where k_r and k_{nr} are the radiative and nonradiative rate constants, the enhancement in the radiative rate must cause a reduction in

TABLE 2: Exciplex (λ_{exc}) and CT Emission Maxima (λ_{CT}) of C_{60}−DMAN/DEAN Systems in Different Solvents

		λ_{exc} (nm)				λ_{CT} (nm)	
solvents[a]	Δf	DMAN	DEAN	solvents	Δf	DMAN	DEAN
DL	0.1108	722	726	DL	0.1108	768	780
HX	0.0931	721	722	HX	0.0931	740	745
CHX	0.1004	721	722	CHX	0.1004	740	745
MCHX	0.1009	722	722	MCHX	0.1009	745	745
0.79% AC[b]	0.1253	725	730	0.65% AC[b]	0.1229	778	790
1.39% AC[b]	0.1353	727	733	1.14% AC[b]	0.1317	790	800
2.78% AC[b]	0.1561	730	738	2.28% AC[b]	0.1493	800	>800
3.73% AC[b]	0.1682			3.04% AC[b]	0.1599	>800	>800

[a] Abbreviations are DL (decalin), HX (*n*-hexane), CHX (cyclohexane), MCHX (methyl cyclohexane), and AC (acetone). [b] Percent of AC is the volume percent of acetone in Decalin.

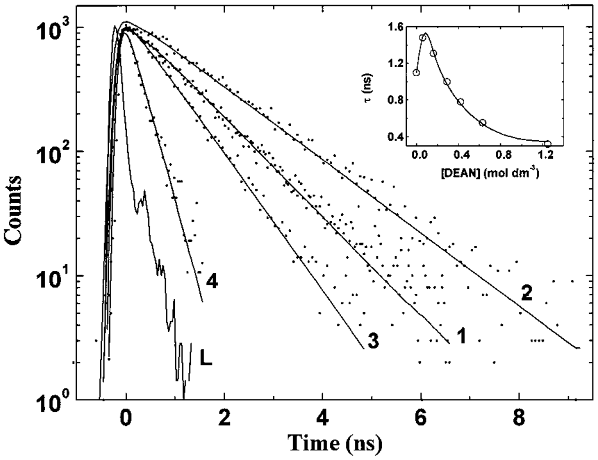


Figure 3. Fluorescence decay curves for C_{60} in Decalin (at 726 nm) with different concentrations (mol dm^{-3}) of DEAN: (1) 0, (2) 0.06, (3) 0.42, (4) 1.25. The curve L is the instrument response function. Inset: variation of τ_f with DEAN concentration.

the fluorescence lifetime of C_{60} in the presence of DMAN/DEAN. Our results of the fluorescence lifetime measurements in Decalin do not go along with this expectation; rather, just like the steady-state fluorescence intensity, the τ_f also initially increases up to a certain concentration of the amine and then decreases again as the amine concentration is further increased. At very high amine concentration (~1.25 mol dm^{-3}), the τ_f more or less attains a minimum plateau value of about 250 ps. The typical time-resolved fluorescence results in DL are shown in Figure 3. Our results on both steady-state and time-resolved fluorescence thus indicate that it must be due to exciplex formation, which causes an enhancement in the fluorescence intensity at the lower concentration range of the added amines. At higher amine concentrations something different must be happening, which we focus in a latter stage.

To see the effect of solvent polarity on the exciplex emission maxima, we measured the emission spectra of C_{60} in a number of AC−DL solvent mixtures, keeping the amine concentration at about 0.16 mol dm^{-3}. The exciplex emission maxima (λ_{exc}) estimated in these solvent mixtures and also in other neat nonaromatic solvents are given in Table 2. The solvent polarity function Δf was estimated as[35]

$$\Delta f = \left(\frac{\epsilon - 1}{2\epsilon + 1}\right) - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right) \tag{4}$$

where ϵ is the dielectric constant and n is the refractive index of the solvent. For pure solvents, ϵ and n values were taken from Lange's handbook.[36] For mixed solvents the dielectric constant (ϵ_{MS}) and the refractive index (n_{MS}) were calculated as[37−39]

$$\epsilon_{MS} = f_A\epsilon_A + f_B\epsilon_B \tag{5}$$

$$n_{MS}^{\ 2} = f_A n_A^{\ 2} + f_B n_B^{\ 2} \tag{6}$$

where the suffixes A and B represent the pure solvents A and B, respectively, and f_A and f_B are the volume fractions of the respective solvents.

The exciplex emission maxima ($\bar{\nu}_{exc}^{max}$) for the C_{60}−DMAN/DEAN systems in different solvents and solvent mixtures have been correlated with the solvent polarity function Δf following eq 7 as suggested by Beens et al.[35]

$$\bar{\nu}_{exc}^{max} = \bar{\nu}_{exc}^{0} - \frac{2\mu^2}{hca^3}\Delta f \tag{7}$$

where $\bar{\nu}_{exc}^{0}$ is the hypothetical gas-phase exciplex emission frequency, μ is the dipole moment of the exciplex, h is the Planck's constant, c is the velocity of light, and a is the interaction distance between the donor and the acceptor in the exciplex. Figure 4 shows the plots of $\bar{\nu}_{exc}^{max}$ vs Δf for C_{60}−DMAN and C_{60}−DEAN systems. Though the experimental fluctuations are quite large, a linear correlation is quite evident from Figure 4. It should also be noted in Figure 4 that solvatochromic behavior of the exciplex emission is carried out only for a very small range of polarity because the exciplex emission could be observed only in this small range of polarity changes. When the polarity is increased beyond this range, the exciplex emission just disappeared, as discussed in a latter paragraph.

The diameter of the C_{60} molecule is about 7 Å.[32] The size of the amine donors were calculated following the Edward's atomic volume addition method,[40] assuming the amine molecules as effective spheres. The average diameter for DMAN and DEAN is estimated to be 6.5 Å. Considering the interaction distance a to be the center-to-center distance between the donor and the acceptor, the value of this parameter is estimated to be 6.75 Å. From the slopes of the plots in Figure 4 and using the above estimate for *a*, the dipole moments of the C_{60}−DMAN and C_{60}−DEAN exciplexes have been estimated to be 10 and 12 D, respectively. It is evident from these μ values that the C_{60}−DMAN/DEAN exciplexes are very polar.

Other interesting points on the C_{60}−DMAN/DEAN exciplexes are as follows. It is seen that in the AC−DL mixed solvent systems, as the AC composition is increased, the exciplex emission intensity (observed with ~0.16 mol dm^{-3} of amines) gradually becomes weaker. In fact, the exciplex emission intensity is very much sensitive to the changes in the AC composition. Thus, the initial increase in the emission intensity as observed in neat DL with amine concentrations of up to about 0.16 mol dm^{-3} (cf. Figure 2) becomes less and less prominent as the AC fraction is gradually increased. The initial

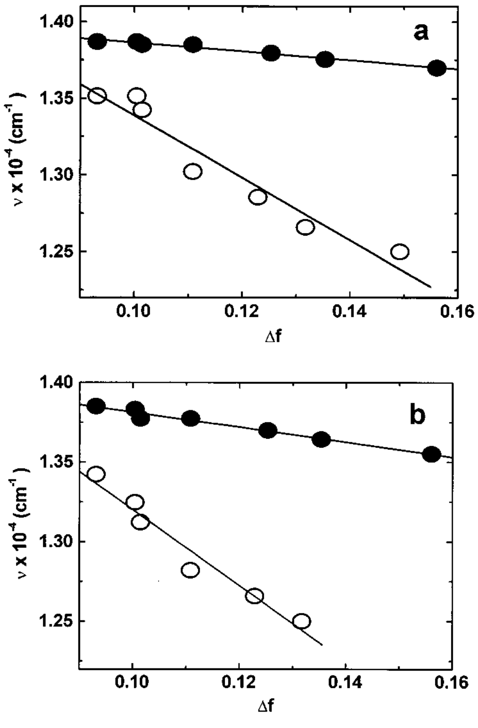


Figure 4. Plot of exciplex (●) and CT (○) emission maxima against the solvent polarity function Δf for (a) C_{60}−DMAN and (b) C_{60}−DEAN systems.

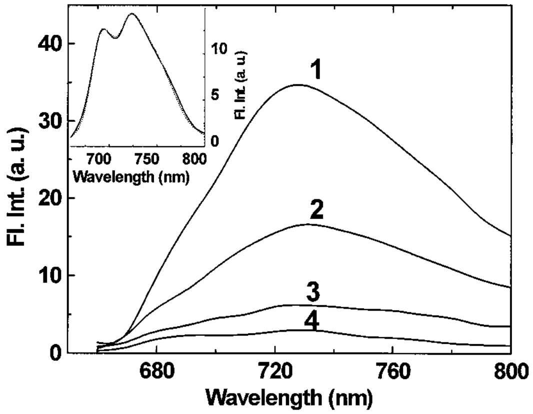
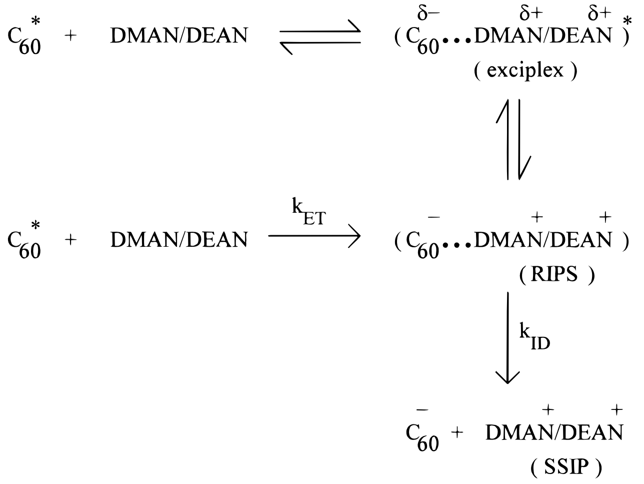


Figure 5. Fluorescence spectra of C_{60} in the presence of 0.16 mol dm^{-3} DEAN in Decalin−acetone solvent mixture: (1) 0%, (2) 1%, (3) 2%, (4) 7% acetone. Inset: Normalized fluorescence spectra of only C_{60} in Decalin (−) and C_{60} in the presence of 0.16 mol dm^{-3} DEAN in 10% acetone−decalin mixture (- - -).

increase is in fact completely absent at ~2% of AC (v/v). Beyond this AC composition the fluorescence intensity of the C_{60}−amine systems just reduces with increasing amine concentration. Similarly, the initial increase in the fluorescence lifetime is also not seen with 2% or more AC composition in DL. Exciplex emission, however, is still indicated from the comparison of the C_{60} emission spectra with and without the amine (0.16 mol dm^{-3}) up to an AC fraction of ~7%. At about 10% AC composition there is no indication of the exciplex emission. The observed emission spectra at these high AC compositions closely resemble that of the C_{60} monomer, though the fluorescence intensity is drastically reduced in comparison to that in the absence of the amines. Figure 5 represents some of these typical results.

It is seen from Figure 1 that at an amine concentration of about 0.16 mol dm^{-3}, there is not much ground-state complex formation. Thus, the photoexcitation process mostly produces

SCHEME 1



the excited state of C_{60} monomers as the first step. In DL or in <3% AC−DL mixed solvents the excited C_{60} monomers form the exciplexes with the amines, and the exciplex emission predominates over the C_{60} monomer emission. At >7% AC−DL mixed solvents the results indicate that there is hardly any exciplex formation, though the excited C_{60} monomers get quenched strongly by the amines.

It is evident from the above results that the C_{60}−DMAN/DEAN exciplexes are very sensitive to the solvent polarity, and this is expected due to the very high dipole moments of these exciplexes (10 and 12 D, respectively). A slight increase in the solvent polarity causes a dramatic reduction in the exciplex emission yield, probably due to the conversion of the exciplexes to the radical ion-pair state (RIPS), which can eventually undergo the ion dissociation (ID) process to give the solvent-separated ion pairs (SSIP).[41,42] In fact the very high dipole moments of the exciplexes indicate that the exciplex and the RIPS could be interconverting to each other even in the nonpolar solvent DL. The reduction in the fluorescence intensity of the exciplexes on increasing the solvent polarity may also be partly due to the direct electron transfer (ET) from the amines to the excited (S_1) fullerenes, producing the RIPS without forming the exciplexes as the intermediates. Thus, the observations with ≤0.16 mol dm^{-3} of amines in C_{60} solutions can be represented by the mechanism in Scheme 1.

In our earlier studies[23,24] of the interaction of the S_1 states of C_{60} and C_{70} with DMAN and DEAN, we observed that in nonpolar but aromatic solvents such as BZ and TOL there was no exciplex formation, though the fluorescence intensity got strongly quenched by the amines. Thus, aromatic solvents behave differently from the nonaromatic solvents. Such an unusual behavior in nonpolar aromatic solvents was tentatively explained by us on the basis of weak ground-state complex formation between the fullerenes and the aromatic solvent molecules via $\pi-\pi$ interaction. Formation of ground-state complexes between the fullerenes and some higher aromatic molecules such as naphthalene, substituted naphthalenes, phenanthrene, and pyrene have also been reported by Ogilby et al.[43] and Sibley et al.[44] Sun et al.,[27,28] however, suggested that in aromatic solvents it was not the ground-state complex formation but rather a direct electron transfer from amines to the excited fullerenes that was responsible for not forming exciplexes in these solvents. According to them, the higher polarizability of the aromatic solvents might energetically support a direct electron transfer rather than the formation of the exciplexes. From our present results in the AC−DL mixed solvent systems

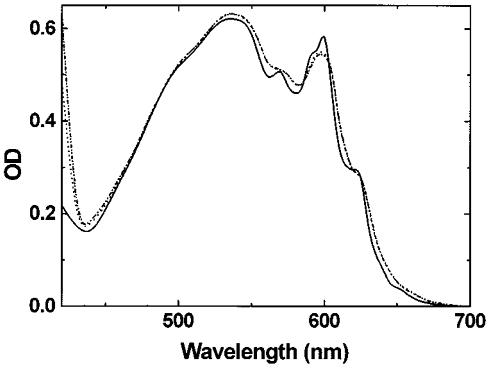


Figure 6. Comparison of the ground-state absorption spectra of C_{60} in benzene (···), toluene (-··) and Decalin (−). $[C_{60}] = 7.24 \times 10^{-4}$ mol dm^{-3}.

it is seen that when the AC composition becomes more than about 7%, there is effectively no exciplex formation; rather, the observed emission spectra resemble very closely that of the C_{60} monomer, though the emission intensity is strongly quenched by the amines. Thus, the observations at >7% AC−DL mixed solvents are very similar to those observed in neat aromatic solvents such as BZ and TOL.[23,24] The solvent polarity function Δf for the 7% AC−decalin mixture is about 0.203. The value for the same polarity function for BZ and TOL is about 0.12, very close to that of DL ($\Delta f = 0.111$). Further, the refractive index values of BZ and TOL are also very similar to that of DL ($n_D = 1.4979$, 1.4941, and 1.4752 for BZ, TOL, and DL, respectively[36]). It is well-known that the refractive index is a measure of the polarizability of a medium. Since in Decalin we observe very efficient exciplex emission, very similar to those in HX ($n_D = 1.3749$[36]), CHX ($n_D = 1.4262$[36]), and MCHX ($n_D = 1.4231$[36]), it is very unlikely that the simple polarizability of the aromatic solvents could be the only reason for not forming exciplexes in these solvents. The basic difference between the solvents DL and BZ/TOL is that the former is nonpolar and nonaromatic whereas the latter is nonpolar but has aromatic π-clouds. It is thus expected that the differences in the behavior of the C_{60}−DMAN/DEAN systems in aromatic solvents such as BZ and TOL in comparison to those in nonpolar nonaromatic solvents such as DL (and also HX, CHX, and MCHX) must be related to the specific $\pi-\pi$ interaction between the fullerenes and the aromatic solvent molecules. To investigate further, we critically compared the absorption spectra of C_{60} in BZ and TOL with that in Decalin as shown in Figure 6. It is seen from this figure that the longest wavelength absorption band of C_{60} in BZ and TOL is almost similar to that in DL except for a slight enhancement in the optical density (OD) at the band maxima (~540 nm) and a little broadening in the vibrational band structures in the aromatic solvents. The 330 nm band of C_{60} (not shown in Figure 6), however, is seen to undergo a substantial change, both in its spectral position as well as in the OD, as the solvent is changed from DL to BZ or TOL. As pointed out in our earlier investigation,[23] these changes are not correlated with the solvent polarizability parameter ($(n^2 - 1)/(n^2 + 2)$) and could be assigned to the formation of the ground-state complexes between the fullerenes and the aromatic solvent molecules.

To have a quantitative estimate for the C_{60}−aromatic (C_{60}−Ar) ground-state complex formation, we added different amounts of BZ to the C_{60} solution in DL. Following the changes in the C_{60} optical density at 336 nm with the BZ concentration (Figure 7), we estimated the ground-state complexation constant K of about 0.2 dm^3 mol^{-1} (Figure 7, inset) following the Benesi−Hildebrand correlation (eq 2). A similar value of K was also estimated for the C_{60}−BZ system in HX.[23] A complexation constant of this order indicates that in neat aromatic solvents the majority of the C_{60} molecules are complexed with the solvent molecules. Thus, the fluorescence of C_{60} in aromatic solvents is expected to be effectively from the excited C_{60}−Ar complexes rather than from the excited (S_1) free C_{60}. Interaction of these excited C_{60}−Ar complexes with amine donors is thus expected to behave differently than those of the excited (S_1) free C_{60}, as observed in nonpolar nonaromatic solvents. It is expected that during interaction of the excited C_{60}−Ar complexes with the aromatic amines there is a solvent-mediated electron transfer from the amine donors to the fullerene acceptors, as shown in Scheme 2, resulting in a strong quenching of the observed fluorescence but without giving any exciplexes as the intermediates. The process of electron transfer in the present systems is thus very similar to the well-known superexchange mechanism suggested for many bridged donor−acceptor systems[45−52] as well as for a number of isolated donor acceptor systems.[53−55]

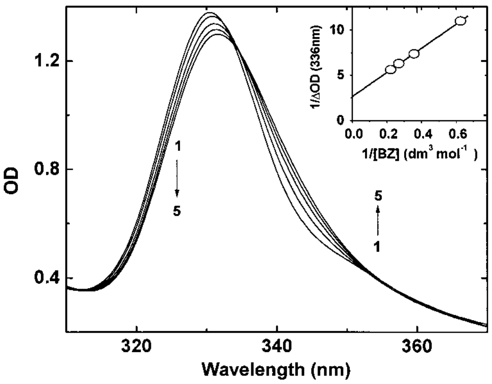
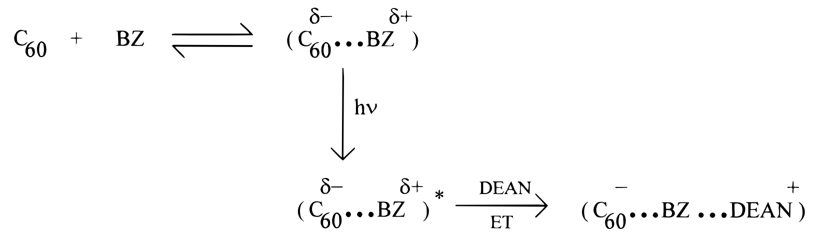


Figure 7. Ground-state absorption spectra of C_{60} in Decalin in the presence of different concentrations (mol dm^{-3}) of benzene (BZ): (1) 0.0, (2) 1.6, (3) 2.8, (4) 3.7, (5) 4.5 mol dm^{-3} of BZ. Inset: Benesi−Hildebrand plot for the calculation of K value for the C_{60}−BZ complex.

Figure 8a shows the comparison of the emission spectra of C_{60} in BZ with that in DL. Though the spectra in both the aromatic and nonaromatic solvents are very overlapping, there are some striking differences. The emission of C_{60} in BZ (and also in TOL) is about 8 nm red-shifted in comparison to that in DL. Since the refractive index[36] and hence the polarizability of DL are very similar to that of BZ (and TOL), such a red shift in the fluorescence spectra in aromatic solvents in comparison to that in DL is not expected. Furthermore, if the polarizability/polarity of the solvents were responsible for these red shifts in the fluorescence spectra, it would be expected that in AC−DL mixed solvents where the solvent polarity is higher than that of BZ/TOL, one should also get similar red shift. Figure 8b compares the emission spectra of C_{60} in DL and 20% AC−DL mixed solvent systems. It is evident from this figure that the differences between the emission spectra are not that prominent as was observed between DL and aromatic solvents. Table 3 lists the emission maxima of C_{60} (λ_{em}^{max}) in different solvent and solvent mixtures. It is seen from this table that even up to an acetone composition of about 20% the λ_{em}^{max} shifts only about 3 nm in comparison to that in DL and other nonpolar nonaromatic solvents. By comparison of the solvent polarity function Δf of a 20% AC−DL mixture with that of BZ and TOL, it is evident that a shift of about 8 nm in the fluorescence maxima of C_{60} in aromatic solvents could not be simply due to the polarity/polarizability of the solvents; rather, it could be related to some specific solute−solvent interactions. It is thus expected that in aromatic solvents the emission mostly originates from the excited C_{60}−Ar complexes rather than from the excited (S_1)

SCHEME 2



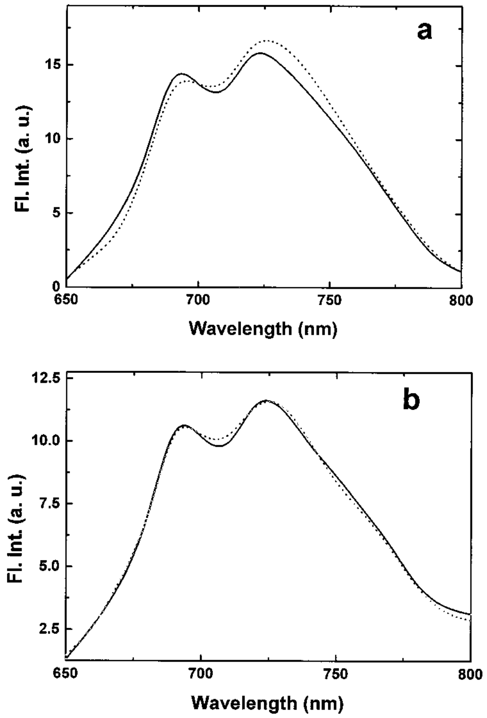


Figure 8. Comparison of the fluorescence spectra of C_{60} (a) in Decalin (—) and in benzene (- - -); (b) in Decalin (—) and in 20% acetone in Decalin (- - -).

TABLE 3: Emission Maxima of C_{60} in Different Solvents

solvents[a]	Δf	λ_{em}^{max} (nm)
HX	0.0931	720
CHX	0.1004	720
MCHX	0.1009	720
BZ	0.1164	728
TOL	0.1268	728
DL	0.1108	720
2% AC[b]	0.1450	721
5% AC[b]	0.1833	723
20% AC[b]	0.2764	723

[a] For abbreviations see footnote of Table 2. [b] The volume percent of acetone in Decalin.

free C_{60} molecules. Since the strength of interaction between C_{60} and the aromatic solvent molecules is weak (because BZ and TOL are weak donors), it is possible that the excited C_{60}−Ar complexes have larger contribution from the C_{60} locally excited state rather than the charge-transfer state, and thus, the emission spectra resemble the C_{60} monomer emission.

At about 0.16 mol dm^{-3} of the amines, the emission spectra in DL and AC−DL mixed solvents are mostly due to the C_{60}−DMAN/DEAN exciplexes. The observed changes in the emission spectra and intensity beyond this concentration of the amines could be due to a number of reasons. It is possible that the exciplexes are quenched by excess amines. If this is the case, the reduction in the fluorescence intensity with the higher amine concentrations is easy to understand. But it is difficult to conceive why the emission maxima should be substantially red-shifted as the amine concentrations are increased beyond 0.16 mol dm^{-3}. If it is argued that with excess amines the initial exciplexes (probably the 1:1 exciplexes) form higher order exciplexes, one can expect a gradual red shift in the emission maxima with higher amine concentrations. The possibility of formation of such higher order exciplexes is, however, expected to be very low, since the concentration of the initial exciplexes is itself very low. Thus, such a dramatic shift (>30 nm) in the emission maxima with amine concentrations beyond 0.16 mol dm^{-3} is very unlikely. Further, if the higher order exciplexes are formed, it should be assumed that the emission efficiency of these exciplexes could be much lower than that of the initial 1:1 exciplexes because the fluorescence intensity is quenched by higher amine concentrations. Thus, in solvents where the initial exciplex emissions are almost negligible, it is very unlikely that there could be any detectable emission from the higher order exciplexes. Figure 9 compares the normalized emission spectra of the C_{60} solutions in 6.7% AC−DL mixed solvent in the presence of about 0.16 and 1.25 mol dm^{-3} DEAN. It is seen from this figure that with 0.16 mol dm^{-3} DEAN there is only nominal emission from the 1:1 exciplexes. At this acetone composition we could also see some emission having fluorescence maxima largely red-shifted in comparison to that of the 1:1 exciplexes with a DEAN concentration of 1.25 mol dm^{-3}. Thus, it is indicated that the red-shifted emission in the presence of higher concentrations of the amines could not be due to the higher order exciplexes. This is more clearly indicated when we plot the intensity ratios at the emission maxima with 0.16 and 1.25 mol dm^{-3} of amines, respectively (i.e., $I_f^{1.25}/I_f^{0.16}$), vs the solvent polarity function (Δf) as shown in Figure 10 for a number of AC−DL mixed solvents. It is seen from Figure 10 that the ratio gradually increases with Δf. In contrast, if the emission at the higher amine concentrations (~1.25 mol dm^{-3}) is due to the higher order exciplexes, it is expected that the $I_f^{1.25}/I_f^{0.16}$ ratio should reduce with Δf because the exciplex emission yield gradually decreases as the solvent polarity is

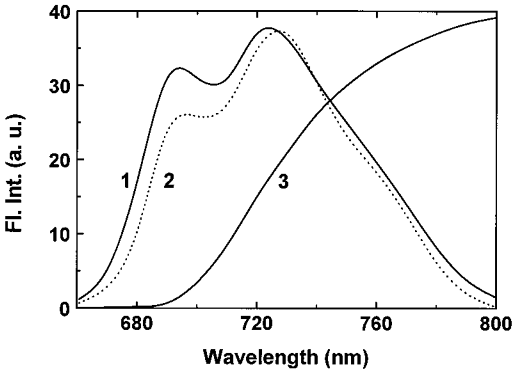


Figure 9. Normalized fluorescence spectra of C_{60} in the presence of different concentrations of DEAN in 6.7% acetone−decalin solvent mixture: (1) 0, (2) 0.16, and (3) 1.25 mol dm^{-3} of DEAN.

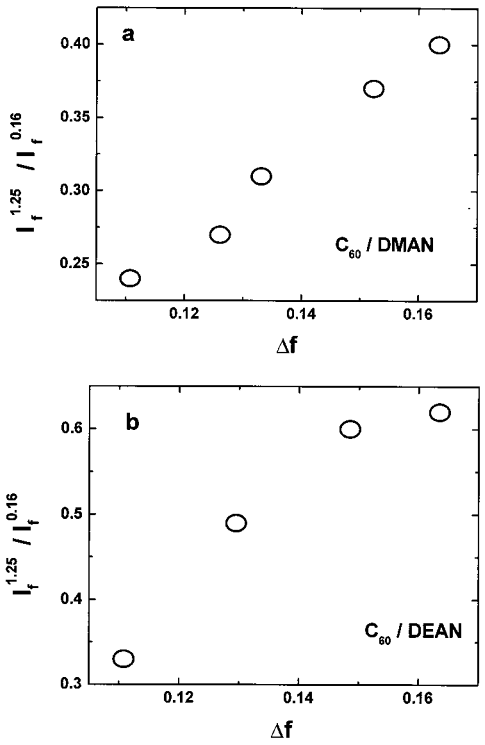


Figure 10. Plot of the ratios of fluorescence intensities at the peak maxima of C_{60} in the presence of 1.25 and 0.16 mol dm^{-3} of (a) DMAN and (b) DEAN with the solvent polarity function Δ*f*.

increased (cf. Figure 5). The results in Figure 10 thus clearly indicate that the higher order exciplexes do not form in the present systems. It is thus assumed that at the higher amine concentrations (greater than ∼0.16 mol dm^{-3} of amines), along with the 1:1 exciplexes, another new emissive species starts contributing. We assume this species to be the excited C_{60}−amine complex.[41,42] As the amine concentration is increased much beyond 0.16 mol dm^{-3}, a good amount of the ground-state C_{60}−amine complexes are formed (cf. Figure 1). These ground-state C_{60}−amine complexes get preferentially excited on irradiation to produce the RIPS state.[41,42] It is probable that the RIPS states in the present systems are very weakly emissive and give very red-shifted fluorescence spectra completely different from that of the exciplex emission spectrum. Such an emission from the RIPS state will henceforth be regarded as the charge transfer (CT) emission. It is expected from the present results that the CT emission efficiency is much lower than that of the exciplex emission.

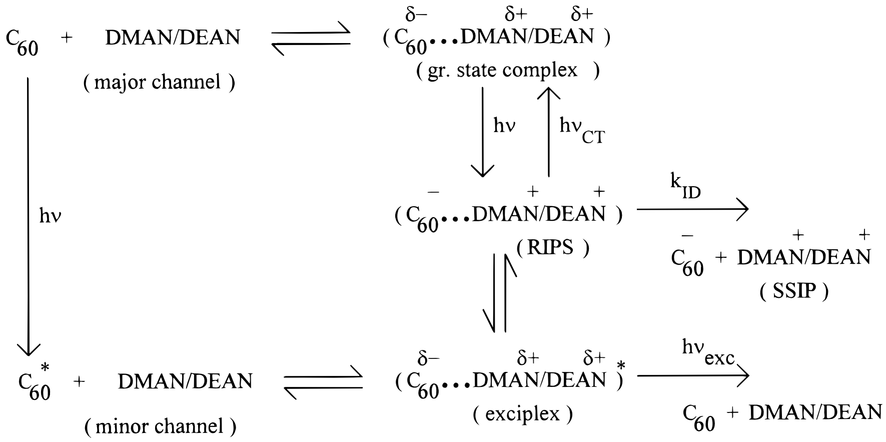
High Amine Conditions. At an amine concentration of about 1.25 mol dm^{-3}, it is evident from Figure 1 that the increase in the OD for the C_{60} solutions is quite substantial due to formation of ground-state C_{60}−amine complexes. It is expected that at this high amine concentration, most of the excitation light (∼75%) must be absorbed by the ground-state complexes. Since even at 1.25 mol dm^{-3} of amines there are some free C_{60}, it is likely that there will be some exciplex formation also, via the excitation of these free C_{60}. However, since the OD values for the ground-state C_{60}−DMAN/DEAN complexes are much higher than that of free C_{60} (cf. Figure 1), it is expected that the RIPS state will be formed predominantly over the exciplexes as shown in Scheme 3. Under this situation it is expected that CT emission (from the RIPS) will dominate the exciplex emission. Such a photoexcitation (Scheme 3) is also supported from our time-resolved fluorescence measurements. As Figure 3 indicates, the fluorescence lifetime for C_{60} initially increases up to a certain amine concentration. This is due to the higher contribution from exciplex emission of higher fluorescence lifetime. As the amine concentration is further increased, the τ_f gradually decreases and ultimately reaches a plateau value. This is supposed to be due to gradually increased contribution of the CT emission, having very low τ_f, as the amine concentration is greatly increased. At very high amine concentration the emission is predominantly from the RIPS, and thus, the τ_f reaches the plateau value corresponding to the lifetime of the CT emission (∼250 ps). Similar results were obtained in other nonpolar nonaromatic solvents (HX, CHX, MCHX, etc.).

The fluorescence maxima observed with ∼1.25 mol dm^{-3} of amines in C_{60} solution were considered as the CT emission maxima. Table 2 lists the CT emission maxima (λ_{CT}) thus obtained for the C_{60}−DMAN/DEAN systems in some neat nonaromatic solvents and AC−DL solvent mixtures. It is seen from Table 2 that the CT emission maxima undergo a larger red shift in comparison to those of the exciplexes as the polarity of the solvent is increased. A plot of the CT emission maxima (ν_{CT}^{max}) versus the solvent polarity function Δ*f* gives a linear correlation as shown in Figure 4. From the slopes of these plots the dipole moments of the excited C_{60}−DMAN/DEAN complexes have been estimated to be about 25 and 27 D, respectively. Considering a complete electron transfer from the amines to the C_{60} molecules in the excited C_{60}−amine complexes and assuming the center-to-center distance of the C_{60} to amine as 6.75 Å, we estimate the dipole moment value to be about 30 D. It is thus indicated that the excitation of the ground-state C_{60}−DMAN/DEAN complexes causes almost a complete electron transfer from the amine to C_{60}. A similar complete charge separation following the photoexcitation of the C_{60}−diphenylamine and C_{60}−triphenylamine complexes have already been observed by us using picosecond laser flash photolysis.[21]

It is seen that the CT emission intensity substantially decreases as the polarity of the solvent is only slightly increased. In fact above ∼7% AC in DL (v/v), we could not detect any CT emission for the C_{60}−DMAN/DEAN systems. Therefore, we could use only a very small range of Δ*f* to investigate the solvatochromism of the CT emission. The reduction in the CT emission intensity with the solvent polarity is assumed to be due to the dissociation of the excited complexes (RIPS) to the solvent-separated ion pairs (SSIP) as indicated in Scheme 3. The reduction in the exciplex emission intensity with the solvent polarity is also supposed to be due to similar kinds of ion dissociation processes via RIPS, as discussed earlier (cf. Scheme 2).

It has been observed that in terms of the CT emission aromatic solvents such as BZ and TOL also behave differently from the other nonpolar nonaromatic solvents. Thus, in the aromatic solvents no CT emission is observed for the C_{60}−DMAN/DEAN systems at an amine concentration of about 1.25 mol dm^{-3}. Since at this higher amine concentration there is a substantial increase in the OD of absorption spectra due to the ground-state complex formation, it is not possible to explain these results in terms of the formation of C_{60}−Ar complexes as discussed with respect to the exciplex emission. To understand the behavior of the aromatic solvents toward the CT emission further, we added different amounts of BZ to the C_{60}−DMAN/DEAN systems in DL with 1.25 mol dm^{-3} of the amines. It is seen that as BZ is added to these solutions, the CT emission intensity is gradually reduced and the emission maxima concomitantly shift to the longer wavelength. Figure 11 shows some of the typical results for the C_{60}−DEAN (1.25 mol dm^{-3}) system in DL with added BZ. It is thus indicated that the aromatic solvents quench the CT emission along with changes

SCHEME 3



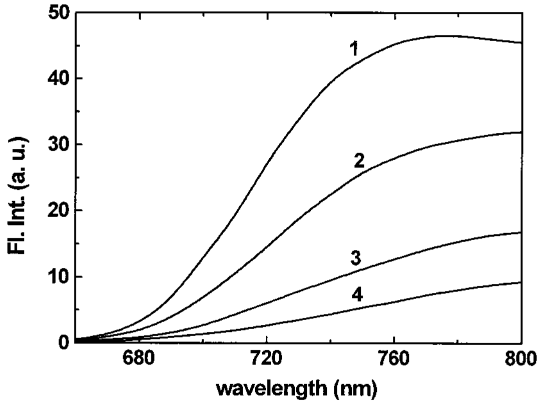


Figure 11. CT emission spectra of C_{60}−DEAN system in Decalin in the presence of different concentrations of benzene (BZ): (1) 0, (2) 1.2, (3) 2.7, and (4) 5 mol dm^{-3} of BZ ([C_{60}] and [DEAN] were kept constant in all the cases).

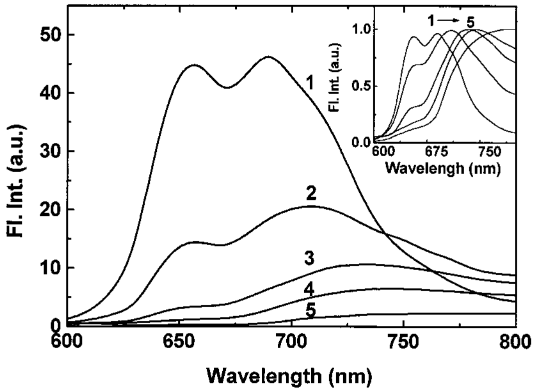


Figure 12. Fluorescence spectra of C_{70} in the presence of different concentrations of DEAN in Decalin: (1) 0, (2) 0.16, (3) 0.42, (4) 0.62, and (5) 1.25 mol dm^{-3} of DEAN. Inset: Spectra 1−5 are presented after normalization to the equal height.

in the shape/maxima of the CT emission spectra. In neat aromatic solvents the quenching is so strong that no CT emission is observed. The red shift of the CT emission maxima with added benzene (cf. Figure 11) is difficult to understand on the basis of the polarity or polarizability of the solvent in comparison to those of DL. It is expected that π-electrons of the aromatic solvents participate in some specific interactions with the present systems, resulting in the quenching of the CT emission as well as in the red shift of the CT emission maxima, though the exact nature of this interaction is not very clear. It may be possible that the π-interactions of the aromatic solvents result in an enhancement in the nonradiative decay channel of the excited CT complexes in the present systems, resulting in a strong quenching of the CT emission. The π-interaction probably enhances the extent of charge separation in the excited CT complexes, causing a red shift in the CT emission maxima with the added aromatic solvents.

3.2.2. C_{70}−DMAN/DEAN Systems. Unlike C_{60}−DMAN/DEAN systems, the C_{70}−DMAN/DEAN systems do not show any unusual increase in the fluorescence intensity in the nonpolar solvents with the added amines. In these systems, however, the exciplex emission is clearly indicated from the comparison of the emission spectra in the presence and in the absence of the amines. Typical spectra are shown in Figure 12. Similar to the C_{60}−DMAN/DEAN systems, the present systems also show a large red shift in the emission spectra at the higher (~1.25 mol dm^{-3}) amine concentrations. These results as well as the solvent polarity effect on the emission spectra are seen to follow qualitatively a similar trend as observed for the C_{60}−DMAN/DEAN systems. Since the ground-state complex formation of C_{70} with the amine donors is as good as that of C_{60}, it is expected that the present systems also follow the mechanistic schemes very similar to Schemes 1 and 3, depending on the concentration of the amine. Unlike the C_{60}−DMAN/DEAN systems, the exciplex emission efficiency, however, is supposed to be weaker for the present systems in comparison to the monomer emission efficiency. In aromatic solvents, the C_{70}−DMAN/DEAN systems also behave similarly to the C_{60}−DMAN/DEAN systems and are expected to be due to the specific interactions of the π-electrons of the solvent molecules with the fullerenes.

Conclusion

The excited (S_1) state of both C_{60} and C_{70} form exciplexes with DMAN and DEAN in nonpolar nonaromatic solvents. At higher amine concentrations the exciplex emission is suppressed by the CT emission arising from the excited fullerene−amine complexes (the RIPS). Both the exciplex and the RIPS are supposed to interconvert to each other in the present systems, though the equilibrium may not be reached instantaneously. Thus, in the low amine concentration range the exciplex emission predominates, whereas in the high amine concentration range the CT emission predominates. It has been observed that for the present systems both the exciplex and the CT emissions are very sensitive to the solvent polarity and are supposed to be due to the high dipole moments of these species. In aromatic solvents neither the exciplex emissions nor the CT emissions are observed for both C_{60}−DMAN/DEAN and C_{70}−DMAN/DEAN systems. These are supposed to be related to the specific interactions of the π-electrons of the aromatic solvent molecules with the fullerenes.

Acknowledgment. The authors are thankful to Prof. N. Periasamy and Mr. M. M. G. Krishna of the Tata Institute of Fundamental Research, Mumbai for their assistance in the time-resolved measurements.

References and Notes

(1) Wang, Y.; Chang, L. T. *J. Phys. Chem*. **1992**, *96*, 1530.

(2) Sension, R. J.; Szarka, A. Z.; Smith, G. R.; Hochstrasser, R. M. *Chem. Phys. Lett*. **1991**, *185*, 179.

(3) Yang, C.; Hwang, K. C. *J. Am. Chem. Soc*. **1996**, *118*, 4693.

(4) Greaney, M. A.; Gorun, S. M. *J. Phys. Chem*. **1991**, *95*, 7142.

(5) Artogast, J. W.; Foote, C. S. *J. Am. Chem. Soc*. **1991**, *113*, 8886.

(6) Nakamura, T.; Tachibina, H.; Yamura, M.; Matsumoto, M.; Azumi, R.; Tanaka, M.; Kawabata, Y. *Langmuir* **1992**, *8*, 4.

(7) Meth, J. S.; Vanherzeele, H.; Wang, Y. *Chem. Phys. Lett*. **1992**, *147*, 26.

(8) Allemand, P. M.; Khemari, K. C.; Koch, A.; Waeld, A.; Holczer, K.; Donovan, S.; Gruner, G.; Thomson, J. D. *Science* **1991**, *253*, 301.

(9) Ebbensen, T. W.; Mochizuki, Y.; Tanigaka, K.; Hiura, H. *Europhys. Lett*. **1994**, *25*, 503.

(10) Catalan, J. *New. J. Chem*. **1995**, *19*, 1233.

(11) Bensasson, R. V.; Bienvenue, E.; Dellinger, M.; L'each, S.; Seta, P. *J. Phys. Chem*. **1994**, *98*, 3492.

(12) Bezmelnitsin, V. N.; Eletskii, A. N.; Stepanov, E. V. *J. Phys. Chem*. **1994**, *98*, 6665.

(13) Picher, T.; Haluska, M.; Winter, J.; Winkler, R.; Burger, B.; Hulman, M.; Kuzmany, H. *Fullerene Sci. Technol.* **1996**, *4*, 227.

(14) Sun, Y. P.; Ma, B.; Bunker, C. E. *J. Chem. Soc., Chem. Commun*. **1994**, 2099.

(15) Huang, H.; Gu, G.; Yang, S.; Fu, J.; Yu, P.; Wong, G.; Du, Y. *Chem. Phys. Lett*. **1997**, *272*, 427.

(16) Xie, Q.; Cordero, E. P.; Echegoych, L. *J. Am. Chem. Soc*. **1992**, *114*, 3978.

(17) Dubois, D.; Kadish, K. M.; Flanagan, S.; Hanfler, R. E.; Chibante, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc*. **1991**, *113*, 4364.

(18) Dubois, D.; Jones, M. T.; Kadish, K. M. *J. Am. Chem. Soc*. **1992**, *114*, 6446.

(19) Nagakawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y.; Koto, T.; Kodama, T.; Oyama, M.; Okazaki, S.; Shida, T. *Chem. Phys. Lett*. **1991**, *186*, 35.

(20) Cox, D. M.; Behab, S.; Disko, M.; Gorum, S.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, T.; Robbins, W.; Sherwood, R. D.; Tindal, P. *J. Am. Chem. Soc*. **1991**, *113*, 2940.

(21) Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P. *J. Am. Chem. Soc*. **1993**, *115*, 11722.

(22) Palit, D. K.; Ghosh, H. N.; Pal, H.; Sapre, A. V.; Mittal, J. P.; Seshadri, R.; Rao, C. N. R. *Chem. Phys. Lett*. **1992**, *198*, 113.

(23) Rao, C. N. R.; Seshadri, R.; Govindaraj, A.; Mittal, J. P.; Pal, H.; Mukherjee, T. *J. Mol. Struct*. **1993**, *300*, 289.

(24) Seshadri, R.; Rao, C. N. R.; Pal, H.; Mukherjee, T.; Mittal, J. P. *Chem. Phys. Lett*. **1993**, *205*, 395.

(25) Allemand, P. M.; Koch, A.; Wadl, F. *J. Am. Chem. Soc*. **1991**, *113*, 1050.

(26) Wang, Y. *J. Phys. Chem*. **1992**, *96*, 764.

(27) Sun, Y. P.; Ma, B. *Chem. Phys. Lett*. **1995**, *236*, 285.

(28) Sun, Y. P.; Bunker, C. E.; Ma, B. *J. Am. Chem. Soc*. **1994**, *116*, 9692.

(29) Ruoff, R. S.; Tse, D. S.; Malhotra, R.; Lorents, C. *J. Phys. Chem*. **1993**, *97*, 3379.

(30) Yarwood, J., Ed. *Spectroscopy and Structure of Molecular Complexes*; Plenum Press: New York, 1993.

(31) Bard, A. J.; Lund, H. *Encyclopaedia of Electrochemistry of the Elements*; Marcel Dekker: New York, 1984; Vol. XV.

(32) Dresselhaus, M. S.; Dressellhaus, G.; Eklund, P. C. *Science of Fullerenes and Carbon Nanotubes*; Academic Press: London, 1996.

(33) Kim, D.; Lee, M. *J. Am. Chem. Soc.* **1992**, *114*, 4429.

(34) Ma, B.; Sun, Y. P. *J. Chem. Soc., Perkin Trans. 2* **1996**, 2157.

(35) Beens, H.; Knibbe, H.; Weller, A. *J. Chem. Phys*. **1967**, *47*, 1183.

(36) Dean, J. A., Ed. *Lange's Handbook of Chemistry*, 13th ed.; McGraw-Hill: New York, 1987.

(37) Masuhara, H.; Hino, T.; Mataga, N. *J. Phys Chem*. **1975**, *79*, 994.

(38) Hirata, Y.; Kanda, Y.; Mataga, N. *J. Phys Chem*. **1983**, *87*, 1662.

(39) Masuhara, H.; Mataga, N. *Acc. Chem. Res*. **1981**, *14*, 312.

(40) Edward, J. T. *J. Chem. Educ*. **1970**, *47*, 261.

(41) Maslak, P. In *Topics in Current Chemistry*; Mattay, J., Ed.; Springer-Verlag: Berlin, 1993; Vol. 168, Chapter 1.

(42) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970; Chapter 9.

(43) Ogilby, P. R.; Scurlock, R. D. *J. Photochem. Photobiol*. *A* **1995**, *91*, 21.

(44) Sibley, S. P.; Nguyen, Y. T.; Campbell, L.; Silber, H. B. *Spectrochim. Acta, Part* A **1997**, *53*, 684.

(45) Miller, J. R.; Beitz, J. V. *J. Chem. Phys*. **1981**, *74*, 6746.

(46) McConnell, H. M. *J. Chem. Phys*. **1961**, *35*, 508.

(47) Liang, C.; Newton, M. D. *J. Phys. Chem*. **1992**, *96*, 2855.

(48) Liang, C.; Newton, M. D. *J. Phys. Chem*. **1993**, *97*, 3199.

(49) Farid, R. S.; Chang, I. Jy.; Winkler, J. R.; Gray, H. B. *J. Phys. Chem*., **1994**, *98*, 5176.

(50) Paddon-Row, M. N. *Acc. Chem. Res*. **1994**, *27*, 18.

(51) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc*. **1994**, *116*, 8176.

(52) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc*. **1994**, *116*, 8188.

(53) McLendon, G. *Acc. Chem. Res*. **1988**, *21*, 160.

(54) Beratan, D. N.; Onuchic, J. N.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *258*, 1740.

(55) Liu, J. Y.; Schmidt, J. A.; Bolton, J. R. *J. Phys. Chem*. **1991**, *95*, 6924.