Photophysical Properties of $C_{60}(C_6H_5)_5Cl$: A Laser Flash Photolysis and Pulse Radiolysis Study

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Photophysical and photochemical properties of the singlet and triplet excited states of monochloropentaphenylfullerene [$C_{60}(C_6H_5)_5Cl$, MCPPF] have been characterized in two different solvents, benzene and benzonitrile, using two complementary transient absorption techniques, namely picosecond laser flash photolysis and nanosecond electron pulse radiolysis. Singlet−singlet and triplet−triplet absorption spectra have been recorded. The quantum yield of triplet formation ($\phi_T = 0.45 \pm 0.05$) and the intrinsic lifetime of the triplet ($\tau = 100 \pm 10\ \mu s$) have been determined. Apart from the intrinsic decay of the triplet to the singlet ground state, another two processes, namely T−T annihilation and quenching by the ground state, make important contribution towards the overal triplet decay rate. Weak charge transfer (CT) complexes are formed between MCPPF and the electron-rich amines diphenylamine (DPA) and triphenylamine (TPA) in benzonitrile solution. On laser excitation, the CT complex undergoes charge separation, but the radical ions undergo very fast geminate recombination to form the triplet state of MCPPF.

Introduction

The unique structure and properties of the newly discovered fullerene [C_{60}], its availability in macroscopic quantities of ultrahigh purity, and its possible applications have created immense interest in the preparation of newer derivatives.[1−6] The functionalization of fullerene has been developed rapidly, and a large number of C_{60} derivatives have been synthesized.[6−12] Many of these derivatives have promising applications in nonlinear optics, optoelectronics, and biological sciences. A significant difference in the optical absorption spectra of the functionalized fullerenes reflect the change in their electronic structure from that of the parent fullerene.[13−16] Consequently, the photophysical and photochemical properties of the functionalized fullerenes too are expected to be affected significantly. Therefore, to find possible applications for these derivatives in different fields of science, it is important to have a detailed understanding about their photophysical and photochemical properties. With this objective, the photophysical and photochemical properties of recently synthesized[17] monochloropentaphenylfullerene (MCPPF) are being reported in this paper.

Experimental Section

Spectroscopic grade benzene and benzonitrile were obtained from Spectrochem, India and were used without any further purification. MCPPF was prepared at the School of Chemistry, Physics and Environmental Science, Unversity of Sussex, U.K. The method of preparation, purification, and characterization of it has been reported elsewhere.[17] All other chemicals were of Analar grade purity. Iolar grade N_2 (Indian Oxygen, 99.9% purity) was used to deaerate the samples prior to pulsed experiments. Steady state optical absorption spectra were recorded on a Hitachi 330 spectrophotometer.

Laser Flash Photolysis. For picosecond laser flash photolysis experiments, the second (532 nm, 5 mJ) or third (355 nm, 3 mJ) harmonic output pulses of 35 ps duration from an active−passive mode-locked Nd:YAG laser (Continuum, Model 501-C-10) used for excitation and continuum probe pulses in the 400−920 nm region were generated by focusing the residual fundamental in the H_2O/D_2O mixture (50:50).[18] The probe was delayed with respect to the pump pulse using a 1 m long linear motion translation stage, and the transient absorption spectra at different delay times (up to 6 ns) were recorded by an optical multichannel analyzer (Spectroscopic Instruments, Germany) interfaced to an IBM-PC. At the zero delay position the probe light reaches the sample just after the end of the pump pulse. Transients surviving beyond 50 ns were studied by monitoring their absorption using a tungsten filament lamp in combination with a Bausch and Lomb monochromator (f/10, 350−800 nm), Hamamatsu R 928 PMT, and a 500 MHz digital oscilloscope (Tektronix, TDS-540A) connected to a PC.

Pulse Radiolysis. High-energy (7 MeV) electron pulses of 50 ns duration generated from a linear electron accelerator were used for pulse radiolysis experiments. The details of the pulse radiolysis setup have been described elsewhere.[19] The transient species produced were detected by monitoring the optical absorption. The absorbed dose was determined by using the aerated KSCN solution with $G\epsilon = 21\,520$ dm^3 mol^{-1} cm^{-1} for 100 eV of absorbed dose (the *G* value is the number of radicals or molecules produced per 100 eV of absorbed energy, and ϵ is the molar absorptivity at 500 nm for the transient $(SCN)_2^{\bullet-}$.

Results and Discussion

Steady State Studies. Figure 1 shows the optical absorption spectrum of MCPPF in cyclohexane. It exhibits a broad absorption band in the region 200−400 nm with two peaks at 232 and 255 nm and shoulders at 340 and 390 nm. The absorption spectrum of C_{60} in cyclohexane has also been provided in Figure 1 for comparison. The absorption peaks of C_{60} at 213, 260, 330, and 405 nm are very sharp as compared to the broad absorption bands of MCPPF in the UV region. In the 450−600 nm region, C_{60} shows a broad low-intensity

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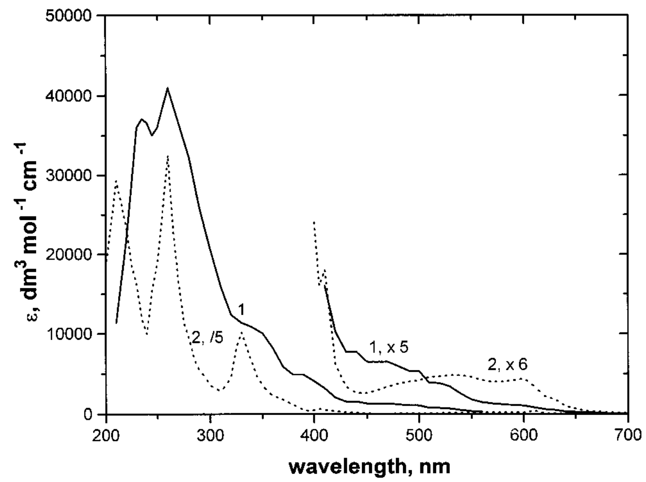

Figure 1. Optical absorption spectra of MCPPF (1) and C_{60} (2) in cyclohexane.

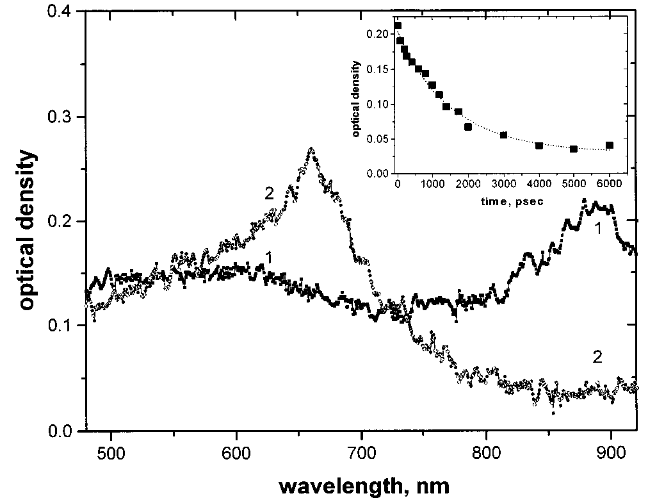

Figure 2. Transient optical absorption spectra obtained on laser flash photolysis (λ_{ex} = 355 nm) of a N_2-saturated solution of MCPPF in benzene at 0 ps (curve 1) and 6 ns (curve 2) after the laser pulse. Inset shows the decay of the transient absorption monitored at 880 nm.

absorption band. However, MCPPF has negligible absorption in this region only with a tail extending up to 600 nm. Also it is important to note that the absorption coefficient of MCPPF has been reduced considerably compared to that of C_{60} throughout the wavelength region 200−650 nm. Hence it is evident that the electronic structure of the parent C_{60} molecule has been considerably distorted due to substitution.

Formation of Excited States. *By Laser Flash Photolysis.* Curve 1 in Figure 2 represents the transient absorption spectrum obtained on laser flash photolysis of a N_2-saturated solution of MCPPF in benzene, immediately after the 35 ps laser pulse of 355 nm. This spectrum may be assigned to the singlet−singlet ($S_1 \rightarrow S_n$) absorption of MCPPF. It shows very broad overlapping absorption bands extending throughout the visible to near IR region (450−900 nm), which can be compared with that of the excited singlet state of C_{60}.[18−21] However, in the present case the singlet spectrum is broader than that of C_{60} . Time-resolved studies showed a growth of the transient absorption at 670 nm and a decay in the region 750−920 nm. Curve 2 in Figure 2, which shows the spectrum obtained at 6 ns after the laser pulse, can be provisionally assigned to the lowest excited triplet state of MCPPF (^{3}MCPPF). The decay of the transient absorption was monitored at 880 nm, and the lifetime of ^{1}MCPPF* obtained was 1.6 ± 0.2 ns (inset of Figure 2). The absorption maxima of ^{3}MCPPF is seen to be blue shifted by ca. 70 nm as compared to that of the triplet state of C_{60}.[18−22]

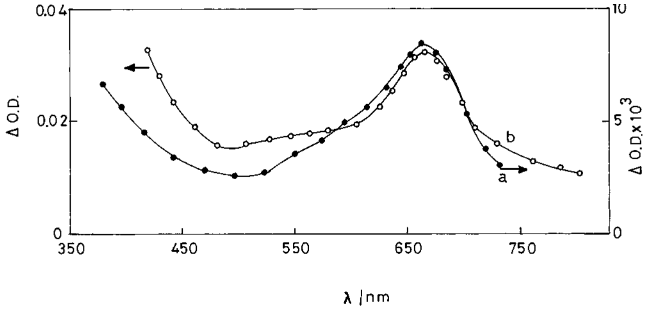

Figure 3. Transient optical absorption spectra obtained on laser flash photolysis (a) and pulse radiolysis (b) of a N_2-saturated solution of MCPPF in benzene.

The characteristics of the transient species of MCPPF were seen to remain unchanged in different solvents (e.g. benzene, benzonitrile) and at different excitation wavelengths (eg 355, 532 nm). The molar absorptivity of ^{1}MCPPF* at 880 nm was determined by comparing its absorbance with that of the benzophenone triplet at 525 nm in acetonitrile (ϵ = 6500 ± 400 dm^3 mol^{-1} cm^{-1}) formed on photoexcitation of their solutions with the same ground state absorbance at 355 nm.[23] Under these conditions, the molar absorptivity of ^{1}MCPPF* at 880 nm was determined to be 9000 ± 1000 dm^3 mol^{-1} cm^{-1}. The molar absorptivity of the C_{60} singlet in benzene at 885 nm has been reported to be 6300 dm^3 mol^{-1} cm^{-1}.[18]

Figure 3a shows the transient optical absorption spectrum obtained by laser flash photolysis (λ_{ex} = 355 nm) of a N_2-saturated solution of MCPPF (8.5×10^{-5} mol dm^{-3}) in benzene recorded 200 ns after the laser pulse. It exhibits a broad absorption band with λ_{max} = 670 nm. The entire spectrum was observed to decay by following first-order kinetics (a detailed analysis of the kinetics is provided later). Confirmation that the spectrum is due to ^{3}MCPPF has been obtained by complete quenching of its absorption in the presence of oxygen and also by β-carotene leading to the formation of the triplet of β-carotene (see later).

By Pulse Radiolysis. The triplet state of a solute can also be generated on pulse radiolysis of a N_2-saturated solution in benzene. The radiolysis of benzene produces its triplet of very high energy (353 kJ mol^{-1}) and with high yield.[23] The triplet state of benzene can transfer its energy to that of another solute having E_T < 353 kJ mol^{-1}, generating the triplet state of the latter. Pulse radiolysis of a N_2-saturated solution of MCPPF (9.5×10^{-4} mol dm^{-3}) in benzene (dose = 47 Gy per pulse) showed a transient absorption band with λ_{max} = 670 nm (Figure 3b). The transient absorption was seen to be efficiently quenched by oxygen. Although this transient spectrum is very similar to that obtained by laser flash photolysis of MCPPF in benzene in the 550−750 nm region, the former shows an increased absorption below 550 nm. This might be due to formation of some adducts, which could not be characterized at present, by high-energy electron irradiation.

Energy Transfer Studies. The conclusive evidence for the formation of a triplet state has been obtained by energy transfer to or from a known triplet which is already well characterized.

Energy Transfer from ^{3}MCPPF to β-Carotene. β-Carotene, which is known to have zero intersystem crossing yield due to direct photoexcitation, forms the triplet state (E_T = 88 kJ mol^{-1}) only by T−T energy transfer from another triplet of higher energy.[23] Also the T−T absorption of the β-carotene triplet has a very high molar absorptivity (1.3×10^5 dm^3 mol^{-1} cm^{-1}) at 515 nm.[23,24] On laser flash photolysis of a N_2-saturated solution of MCPPF (4×10^{-4} mol dm^{-3}) in benzene, the transient absorption (λ = 670 nm) was observed to decay faster on addition of β-carotene (4×10^{-5} mol dm^{-3}). Simulta-

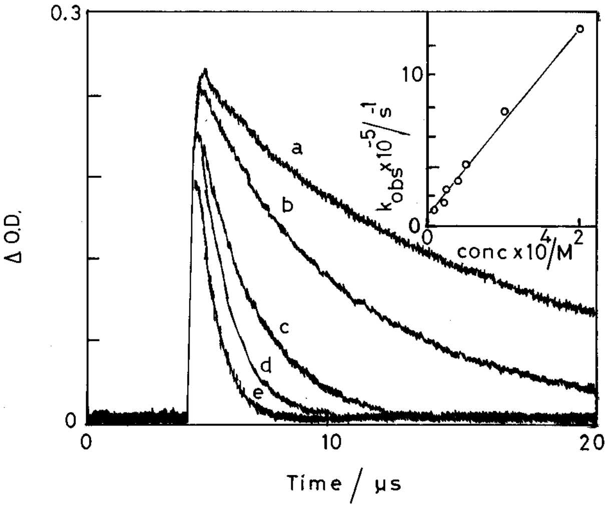

Figure 4. T−T absorption decay on pulse radiolysis of *p*-terphenyl (1×10^{-2} mol dm^{-3} , $\lambda = 460$ nm) in the presence of 0 (a), 0.3 (b), 0.8 (c), 1 (d), and 2×10^{-4} mol dm^{-3} (e) MCPPF. Inset shows the variation of k_{obs} with the concentration of MCPPF used in the quenching experiment.

neously, the absorption at 515 nm, which is characteristic of the triplet state of β-carotene, was observed to grow. These studies suggest that the 670 nm band (Figure 3), formed on laser flash photolysis of MCPPF in benzene, is due to its triplet state and that its energy level is higher than that of β-carotene.

The molar absorptivity of ^{3}MCPPF at 670 nm was determined from the energy transfer experiments following the method suggested by Amouyal et al.[24] The value was found to be 25 000 dm^3 mol^{-1} cm^{-1} after applying the necessary corrections for the participation of other processes apart from the energy transfer process.[25]

The energy transfer to β-carotene from the pulse radiolytically produced triplet state of MCPPF was also investigated in a N$_2$-saturated benzene solution of MCPPF, and the molar absorptivity at 670 nm has been determined to be 20 000 dm^3 mol^{-1} cm^{-1}.The value is in reasonably good agreement with that determined from laser flash photolysis experiments, and an average value of the molar absorptivity of ^{3}MCPPF can be taken as 22 000 ± 2500 dm^3 mol^{-1} cm^{-1}. Hence the molar absorptivities of both the singlet and triplet states of MCPPF are higher than those of C$_{60}$ (6300 and 12 000 dm^3 mol^{-1} cm^{-1}, respectively).[18]

Energy Transfer to MCPPF. The energy transfer processes from the triplet state of higher energy donors, e.g., *p*-terphenyl ($\lambda_{max} = 460$ nm, $\epsilon_T = 90\,000$ dm^3 mol^{-1} cm^{-1}, $E_T = 244$ kJ mol^{-1}) and biphenyl ($\lambda_{max} = 360$ nm, $\epsilon_T = 27\,100$ dm^3 mol^{-1} cm^{-1}, $E_T = 274$ kJ mol^{-1}),[23,24] to ^{3}MCPPF have also been studied. The triplets of *p*-terphenyl or biphenyl were generated on pulse radiolysis of a N$_2$-saturated solutions in benzene. For these studies, the concentration of the donor was kept at 1×10^{-2} mol dm^{-3} and that of the acceptor MCPPF was varied from (0−2) × 10^{-4} mol dm^{-3}. Under these conditions, only the triplets of the donors were initially produced, which in turn transferred energy to the acceptor. The decay of the donor triplet was monitored as a function of MCPPF concentration. The pseudo-first-order decay (k_{obs}) of the *p*-terphenyl triplet became faster as the concentration increased (Figure 4), suggesting energy transfer from ^{3}(*p*-terphenyl) to ^{3}MCPPF. The energy transfer rate was determined from the plot of k_{obs} vs MCPPF concentration (inset of Figure 4), and the value was calculated to be 6.1×10^9 dm^3 mol^{-1} s^{-1}. Time-resolved spectra recorded at 15 μs after the pulse showed the formation of ^{3}MCPPF (Figure 5).The rate constant for energy transfer from the biphenyl triplet to ^{3}MCPPF was determined to be 5.2×10^9 dm^3 mol^{-1} s^{-1}.

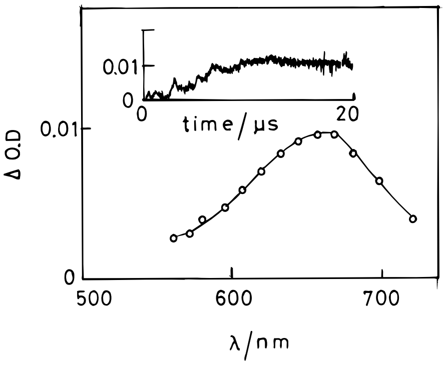

Figure 5. Transient optical absorption spectrum obtained on pulse radiolysis of a N$_2$-saturated solution of *p*-terphenyl (1×10^{-2} mol dm^{-3}) containing MCPPF (2×10^{-4} mol dm^{-3}) 15 μs after the pulse. Inset shows the growth of ^{3}MCPPF monitored at 670 nm.

The triplet state of anthracene has an energy level of 178 kJ mol^{-1} ($\lambda = 430$ nm, $\epsilon = 71\,500$ dm^3 mol^{-1} cm^{-1}).[23,24] No transfer of energy from the pulse radiolytically generated triplet of anthracene to ^{3}MCPPF or vice versa could be observed by us. This suggests that the triplet energy level of MCPPF is close to 178 kJ mol^{-1}, which is slightly higher than those of C$_{60}$ and C$_{70}$ (151 and 148 kJ mol^{-1}).[21]

Quantum Yield of ^{3}MCPPF. Using the values of extinction coefficient for singlet and triplet absorptions at 880 and 670 nm, respectively, the quantum yield of triplet formation can be easily calculated by comparing their absorbance values at these two wavelengths, as shown in Figure 2. The quantum yield value was determined to be 0.45 ± 0.05. The absorbance of ^{3}MCPPF at 670 nm, formed on pulse radiolysis of a N$_2$-saturated solution of MCPPF (8.6×10^{-5} mol dm^{-3}) in benzene at various dose rates (29−163 Gy per pulse), was determined, and *G*(^{3}MCPPF) was calculated to be 0.15 ± 0.02.

Decay Kinetics of ^{3}MCPPF. The decay kinetics of ^{3}MCPPF was seen to be extremely sensitive to the concentration of MCPPF used and also to the laser intensity used for excitation, i.e., the concentration of ^{3}MCPPF produced. Hence it is expected that, in addition to the normal first-order decay of ^{3}MCPPF to the ground state (eq 1), other possible processes contributing to the decay of ^{3}MCPPF might be triplet−triplet annihilation (eq 2) and quenching of the ^{3}MCPPF by the ground state MCPPF (eq 3).

$$^3\mathrm{MCPPF} \xrightarrow{k_T} {}^1\mathrm{MCPPF} \qquad (1)$$

$$^3\mathrm{MCPPF} + {}^3\mathrm{MCPPF} \xrightarrow{k_{TT}} 2\,{}^1\mathrm{MCPPF} \qquad (2)$$

$$^3\mathrm{MCPPF} + {}^1\mathrm{MCPPF} \xrightarrow{k_{TS}} 2\,{}^1\mathrm{MCPPF} \qquad (3)$$

The rate constants for T−T annihilation (k_{TT}) and self-quenching (k_{TS}) have been determined as follows:

The self-quenching rate constant (k_{TS}) for the photolytically generated ^{3}MCPPF was determined by monitoring its decay at 670 nm for various concentrations of MCPPF [(0.5−8.6) × 10^{-5} mol dm^{-3}] using the same laser energy for excitation. The life time of ^{3}MCPPF increased from 13.1 to 65 μs when the concentration of MCPPF was reduced from 8.6×10^{-5} mol dm^{-3} to 0.5×10^{-5} (Figure 6). The rate constants thus obtained were plotted against the concentration of MCPPF (inset of Figure 6). The quenching rate constant (k_{TS}) thus determined, from the slope of the least square fit line, was 7.8×10^8 dm^3 mol^{-1} s^{-1}. The value of the rate constant obtained by extrapolation of the least square fit line up to zero concentration

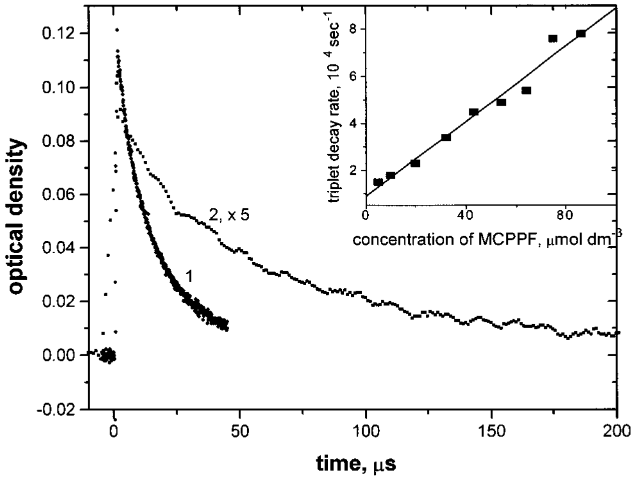

Figure 6. Decay traces for the transient absorption due to the triplet monitored at 670 nm with a MCPPF concentration of 0.5 × 10^{-5} (1) and 8.6 × 10^{-5} mol dm^{-3} (2). The inset shows the plot of the observed triplet decay rate vs the concentration of MCPPF.

of MCPPF was found to be 0.9 × 10^4 s^{-1}, which can be taken as the value of k_T, the triplet decay rate constant. The inverse of k_T should be the actual lifetime ($\tau = 110$ μs) of ^{3}MCPPF in the absence of reactions 2 and 3.

The triplet−triplet annihilation rate constant (k_{TT}) was determined by monitoring the decay of ^{3}MCPPF as a function of laser pulse energy at a fixed concentration of MCPPF (8.6 × 10^{-5} mol dm^{-3}). The concentration of ^{3}MCPPF initially formed was determined by comparing the absorbance of the benzophenone triplet at 525 nm ($\epsilon = 6500$ dm^3 mol^{-1} cm^{-1}) with that of ^{3}MCPPF at 670 nm formed on photoexcitation of their solutions with the same ground state absorbance at 355 nm. The lifetime of ^{3}MCPPF increased from 12.4 to 21.2 μs when the ^{3}MCPPF concentration decreased from 6.1 × 10^{-6} to 1.3 × 10^{-6} mol dm^{-3}. The value of k_{TT} thus determined from the slope of the linear plot of the observed rate constant vs ^{3}MCPPF concentration was 6 × 10^9 dm^3 mol^{-1} s^{-1} .

The self-quenching rate constant (k_{TS}) for the pulse radiolytically (dose = 52 Gy per pulse) generated ^{3}MCPPF was determined by monitoring the decay of ^{3}MCPPF at 670 nm for various concentrations of MCPPF [(1.5−9.0) × 10^{-5} mol dm^{-3}]. The value of k_{TS} and the lifetime were determined to be 3.8 × 10^8 dm^3 mol^{-1} s^{-1} and 95 μs, respectively. The triplet−triplet annihilation rate (k_{TT}) was determined to be 1 × 10^{10} dm^3 mol^{-1} s^{-1} in the dose rate range 29−163 Gy per pulse. The values of k_{TS}, k_{TT}, and the intrinsic lifetime (τ) determined in pulse radiolysis and laser flash photolysis experiments are in reasonable agreement with each other.

Formation of Charge Transfer Complexes. *Steady State Studies.* The optical absorption spectrum of MCPPF (1.07 × 10^{-4} mol dm^{-3}) in benzonitrile showed increased absorption in the region 350−550 nm on addition of 1 mol dm^{-3} diphenylamine (DPA). DPA in benzonitrile has very little absorption at $\lambda > 400$ nm. C_{60}, which has a high electron affinity (2.6−2.8 eV),[26] is known to form a charge transfer (CT) complex with electron-rich amines in the ground state.[27] Therefore, the increased absorption on addition of DPA may be due to the formation of a ground state CT complex (eq 4) between MCPPF and DPA. Considering the formation of a 1:1 complex in the ground state, the Benesi−Hildebrand equation was applied to determine the molar absorptivity (ϵ_{DA}) and the equilibrium constant (K) for the complex **DA**.[28]

$$\underset{\textbf{(A)}}{\text{MCPPF}} + \underset{\textbf{(D)}}{\text{DPA}} \rightarrow \underset{\textbf{(DA)}}{\text{MCPPF}^{\delta-}\text{−DPA}^{\delta+}} \qquad (4)$$

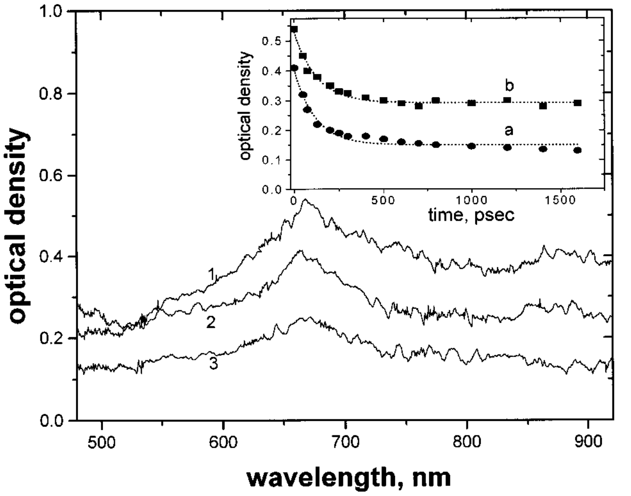

Figure 7. Time-resolved transient optical absorption spectra obtained on laser flash photolysis of MCPPF (6.5 × 10^{-4} mol dm^{-3}) + TPA (1 mol dm^{-3}) in benzonitrile recorded at 0 (1), 66 (2), and 900 ps (3) after the pulse. The inset is the transient absorption decay monitored at 880 nm (a) and 670 nm (b).

These values are found to be 4.67 × 10^3 dm^3 mol^{-1} cm^{-1} and 0.625 dm^3 mol^{-1}, respectively for the MCPPF−DPA complex. Similar studies have been carried out with triphenylamine (TPA) as the donor, and the values of ϵ_{DA} and K are 9.3 × 10^3 dm^3 mol^{-1} cm^{-1} and 0.3 dm^3 mol^{-1}, respectively. In benzene, the changes in the absorption spectra of MCPPF on addition of DPA or TPA were very small. The charge separation is facilitated by the higher dielectric constant of benzonitrile, and therefore, the relatively stronger complex is formed in benzonitrile rather than in benzene.

Time-Resolved Studies. The dynamics of charge transfer in the excited CT complex was investigated by picosecond laser flash photolysis on excitation at 532 nm, which does not excite the amine directly. Biphotonic ionization of these amines was also avoided by keeping the laser energy low. Blank experiments with the solutions containing only amines in benzonitrile were also performed under similar conditions to ensure that cation radicals were not formed via biphotonic ionization of the amines.

Figure 7 shows the time-resolved transient absorption spectra obtained on picosecond laser flash photolysis of the MCPPF−TPA complex. The spectrum recorded immediately after the laser pulse (curve 1) was seen to be different from that obtained on laser flash photolysis of MCPPF in benzonitrile solution. The former, in spite of its broad feature, can be characterized by two distinct bands with maxima at ca. 670 and 880 nm. The transient absorbance at 880 nm was seen to follow first-order kinetics with a lifetime of 130 ± 25 ps to decay to a longer lived transient species (curve a in the inset of Figure 7). This lifetime value is much shorter than the lifetime (1.6 ns) of the singlet state of MCPPF. Hence the red band can be assigned either to ^{1}MCPPF* being quenched by TPA or to the anion radical of MCPPF (MCPPF$^{\bullet-}$), which undergoes geminate recombination with its counterion, TPA$^{\bullet+}$, formed due to charge separation in the excited state of the CT complex. However in the latter case we should observe the absorption due to TPA$^{\bullet+}$ too. The absorption spectrum of free TPA$^{\bullet+}$ is known to have a maxima at 620 nm in benzonitrile solution.[28] However, in our earlier studies on the charge separation process in the C_{60}−TPA complex, we have observed an absorption peak due to the $C_{60}^{\bullet-}$−TPA$^{\bullet+}$ radical ion pair in benzonitrile at ca. 660 nm.[27] Hence the absorption peak observed here at 670 nm, which is ca. 50 nm red shifted with respect to the absorption maximum of free TPA$^{\bullet+}$, can be assigned to TPA$^{\bullet+}$ in the radical ion pair

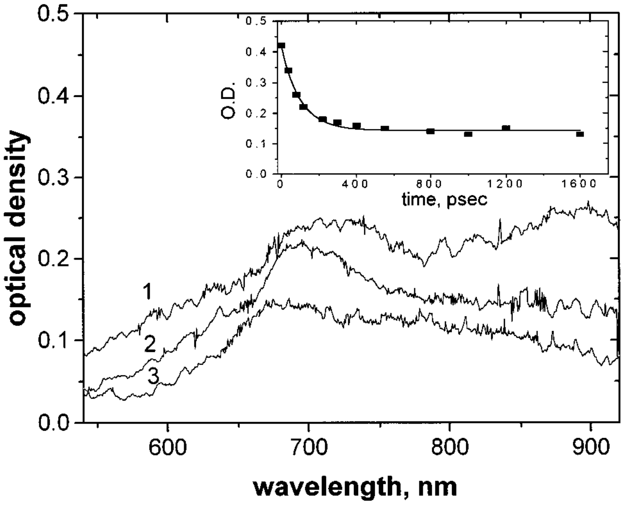

Figure 8. Time-resolved transient optical absorption spectra obtained on laser flash photolysis of MCPPF (6.5×10^{-4} mol dm^{-3}) + DPA (1 mol dm^{-3}) in benzonitrile recorded 0 (1), 66 (2), and 1950 ps (3) after the pulse. The inset is the transient absorption decay monitored at 880 nm.

MCPPF$^{\bullet-}\cdots$TPA$^{\bullet+}$, formed due to excitation of the CT complex. Possibly due to its strong association with the fullerene molecule in the CT complex, the absorption peak of the radical cation showed this shift. This is confirmed by the fact that the absorbance at 670 nm too decays at the same rate as that at 880 nm (curve b in the inset of Figure 7). The transient spectrum recorded after 900 ps shows the presence of a single band at 670 nm and could be assigned to ^{3}MCPPF formed on geminate recombination of the radical ion pair.

Figure 8 shows the time-resolved absorption spectra of the transient produced due to picosecond laser flash photolysis of the MCPPF−DPA complex in benzonitrile solution. The spectrum recorded at 0 ps (curve 1) shows two major peaks at 710 and 880 nm. Time-resolved studies showed that the transient absorbance at 880 nm decays very fast with a lifetime of ~300 ps to another transient which survives beyond 2 ns. The other band at 710 nm gradually shifted to 670 nm after 1.6 ns. Considering these facts, the transient absorption peak at 710 nm observed at 0 ps may be assigned to DPA$^{\bullet+}$ in the radical ion-pair MCPPF$^{\bullet-}\cdots$DPA$^{\bullet+}$, and that at 880 nm, to MCPPF$^{\bullet-}$ and ^{1}MCPPF* which is formed due to direct excitation of the free MCPPF in solution. The transient absorption maximum at 670 nm observed at 1.6 ns (curve c in Figure 8) can be assigned to ^{3}MCPPF, the formation of which has been followed by the geminate recombination of the radical ion pair, but this transient absorption spectrum also shows some residual absorption at 880 nm, indicating the presence of ^{1}MCPPF* surviving even after the geminate recombination of the radical ion pair. However, the free ion yield in both cases investigated is negligible, and hence the geminate recombination leading to the formation of the triplet and radiationless deactivation to recover the ground state CT complex are the dominant processes the ion pairs undergo in the excited CT complex.

Conclusions

We have presented a detailed study of the photophysical and photochemical properties of MCPPF, a monocholoropentaphenyl derivative of Buckminister fullerene, C_{60}. Due to substitution, many of the photophysical properties, e.g., optical absorption of the ground and excited states, have been significantly affected. Also the quantum yield of triplet formation, which is unity for C_{60}, has been reduced to about 50%. However, the absorption coefficients for both the singlet and triplet states have been seen to be higher for MCPPF than that of C_{60}. These properties along with the very long lifetime (~100 μs) of the triplet promise its use as an important material for the optical limiting switch which is currently being investigated in our laboartory. We have also investigated its electron transfer reactions with electron-rich aromatic amines, which have not been siginificantly affected due to substitution.

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