ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 21–25

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Excited-state charge-transfer complexes formed between C_{60} and substituted naphthalenes

Rodger D. Scurlock, Peter R. Ogilby *

Department of Chemistry, University of New Mexico, Albuquerque, NM 87131, USA

Received 19 January 1995; accepted 24 May 1995

Abstract

Solutions of the fullerene C_{60} and a substituted naphthalene give rise to a new absorption band that is not observed from solutions containing only C_{60} or the naphthalene. The absorption maximum of this new band successively shifts to a longer wavelength as the ionization potential of the naphthalene decreases. These data reflect a C_{60}–naphthalene cooperative absorption from a ground-state contact complex to form an excited-state complex with charge-transfer character. This excited-state C_{60}–naphthalene complex decays to yield the localized C_{60} singlet excited state which, in turn, yields the C_{60} triplet state with approximately unit efficiency.

Keywords: C_{60}; Charge-transfer complex

1. Introduction

In the course of recent experiments in which the fullerene C_{60} was used as a singlet oxygen photosensitizer [1], we recorded the C_{60} absorption spectrum in a variety of solvents (acetone, n-heptane, $C_6H_5CF_3$, 1,4-dioxane, dichloromethane, cyclohexane, benzene, bromobenzene, iodobenzene and carbon disulfide). Although we observed solvent-dependent spectral shifts of less than ~4 nm on the C_{60} absorption profile, the general features of the spectrum, as described by Leach et al. [2] and Hare et al. [3], were independent of the medium in which C_{60} was dissolved. These C_{60} solutions were purple owing to absorption bands between 450 and 630 nm. However, when C_{60} was dissolved in the colorless liquid 1-methylnaphthalene, the solution appeared yellow–red, not purple, and the absorption spectrum showed a distinct feature that had previously not been observed in other solvents. This effect was also observed for other substituted naphthalenes.

Changes in the absorption spectrum of solution-phase C_{60} have been observed when amines are co-dissolved with the C_{60} [4–9]. However, these changes appear principally as amine-enhanced C_{60} transitions; the intensity of the 450–650 nm C_{60} band increases on addition of the amine. To our knowledge, there have been no reports of discrete new absorption bands for solutions of C_{60} dissolved with an additional solute. In the present work, we used ground-state absorption, flash absorption and emission spectroscopy to examine various aspects of the C_{60}-substituted naphthalene interaction.

2. Experimental

The experiments were performed with C_{60} obtained from three different sources: Aldrich, Fischer and MER. The C_{60} was used as received. Naphthalene (Aldrich Gold Label) was used as received. The substituted naphthalenes (Aldrich) were purified by chromatography on silica gel as described previously [10].

Ground-state absorption spectra were recorded on a Beckman DU-40 spectrophotometer using 1 cm path length cells. In all cases, the spectrum of liquid toluene was used as a background. In addition, the spectrum of naphthalene (1.8 M) was subtracted from the spectrum recorded from a solution of C_{60} co-dissolved with naphthalene.

Flash absorption spectra were obtained using instruments and techniques that have already been described [10,11]. Briefly, both the second (532 nm) and third (355 nm) harmonics of the Nd:YAG fundamental lasing wavelength were used for sample excitation. In addition, the first Stokes line obtained by stimulated Raman scattering of 355 nm in hydrogen gas allowed us to excite samples at 416 nm. A 150 W xenon lamp was the probe source. The detector used was a

---

* Corresponding author.

SSDI 1010-6030(95)04123-0

silicon diode whose response function was exponential with a lifetime of 100 ns.

Emission spectra were recorded using a Perkin-Elmer LS-5 spectrometer.

3. Results and discussion

3.1. Ground-state absorption spectra

Absorption spectra recorded in toluene solvent are shown in Fig. 1. The spectrum of C_{60} at 1×10^{-4} M is consistent with that previously reported [2,3]. At 1.8 M, the naphthalenes do not absorb at wavelengths longer than ~400 nm (nevertheless, for the data shown in Fig. 1, the naphthalene spectrum was subtracted from the corresponding spectrum of that naphthalene co-dissolved with C_{60}). When 1×10^{-4} M C_{60} is co-dissolved with 1.8 M 1-chloronaphthalene (CN), absorption in the spectral region ~390–460 nm increases relative to that observed from the C_{60} solution lacking the naphthalene. Spectra of C_{60} co-dissolved with naphthalene (N) and 1-bromonaphthalene (BN) are very similar to that recorded from the C_{60}–CN solution. In a mixture of 1×10^{-4} M C_{60} and 1.8 M 1-methylnaphthalene (MN), an absorption is observed in the spectral region ~390–500 nm that is (a) more pronounced and (b) red-shifted relative to data recorded from the C_{60}–CN solution. Finally, when 1×10^{-4} M C_{60} is co-dissolved with 1.8 M 1-methoxynaphthalene (MON), a distinct absorption band in the region ~420–520 nm becomes apparent. In all cases, because the 405 and 600 nm C_{60} bands do not shift in wavelength with added naphthalene, naphthalene-dependent changes in a given spectrum are consistent with the superposition of a second absorption profile on the C_{60} spectrum.

Difference spectra were obtained from the data in Fig. 1 by subtracting the C_{60} spectrum from the spectrum of C_{60} co-dissolved with the naphthalene (Fig. 2). Distinct bands were observed with maxima at ~390, 425 and 450 nm for the solutions containing CN, MN and MON, respectively. At wavelengths below ~420 nm, the apparent structure on the difference spectra reflects the fact that discrete C_{60} absorption bands (e.g. the band at 405 nm) are slightly broadened by the presence of the naphthalene. Nevertheless, on the basis of the absorbance data shown in Fig. 1, we feel that the general profile of these difference spectra are accurate to wavelengths as short as ~380 nm.

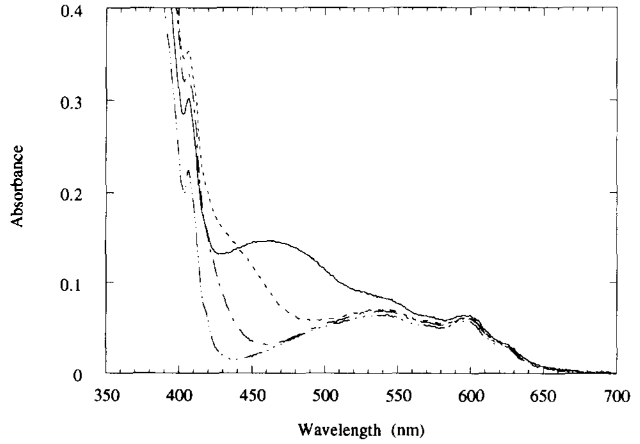


Fig. 1. Absorption spectra recorded in toluene: C_{60} at 1×10^{-4} M (–···–), C_{60}+CN (– – –), C_{60}+MN (---) and C_{60}+MON (——). In each case, the naphthalene concentration is 1.8 M.

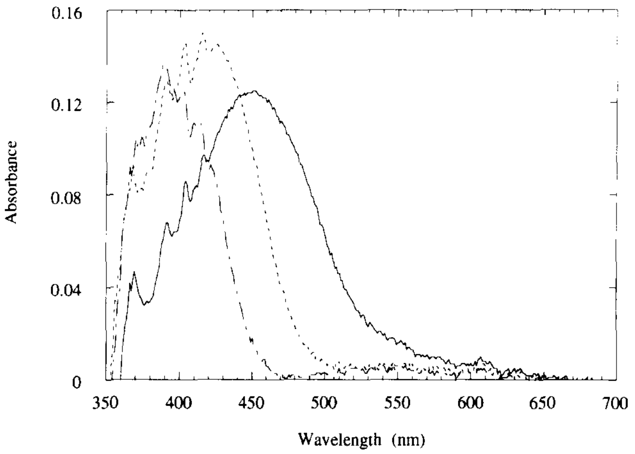


Fig. 2. Difference spectra obtained from Fig. 1 by subtracting the C_{60} spectrum from (1) the C_{60}+CN spectrum (– – –), (2) the C_{60}+MN spectrum (---) and (3) the C_{60}+MON spectrum (——).

Our data are consistent with (a) formation of a ground-state complex between C_{60} and the naphthalene and (b) a transition in which an excited state of the C_{60}–naphthalene complex is populated. The adiabatic ionization potentials of N, CN, BN, MN and MON are 8.14, 8.13, 8.09, 7.85 and 7.70 eV, respectively [12,13]. The λ_{max} of the new absorption band [1] successively shifts to a longer wavelength as the ionization potential of the naphthalene decreases. Therefore, it is likely that at least the excited state populated by absorption of light has charge-transfer (CT) character in which the naphthalene acts as an electron donor. Although the ground state may also have some CT character, the data indicate that the amount of such character cannot impart an attractive interaction between C_{60} and the naphthalene that exceeds a corresponding interaction in the excited state (i.e. the energy gap between the ground and excited states must decrease with an increase in CT character). Such a condition can be met if the ground state acquires CT character from an excited state via configuration interaction [14].

Ground-state complexes between C_{60} and electron donors have been observed in solid-phase and crystalline samples [9,15–18]. In solution, changes in the ground-state absorption spectrum have been observed when a variety of amines are co-dissolved with C_{60} [4–9]. Seshadri et al. [7] suggested that these changes may indicate an amine-enhanced C_{60} transition. Certainly, discrete bands separate from those of C_{60}, such as those shown in Figs. 1 and 2, are not apparent

---

[1] We also used the wavelength at which the absorbance of the respective difference spectra equals a given value (e.g. 0.05).

in the C_{60}–amine spectra. Nevertheless, it has been proposed that a weak ground-state complex is formed in these systems which, in turn, can absorb light to populate a CT state.

Rao and co-workers also proposed that C_{60} forms a ground-state complex with molecules that contain an aromatic π system [7,8]. In this case, however, the supporting evidence is not particularly pronounced. In brief, they examined the effect of solvent on the ~330 nm absorption band of C_{60} and noted that the λ_{max} for this band in benzene, toluene, *p*-xylene and mesitylene was red shifted by about 4 nm relative to that observed in cyclohexane. Furthermore, they showed that this red shift was about 2 nm greater than what would be expected solely on the basis of a change in the solvent polarizability. Although the C_{60} λ_{max} in benzene did not differ from λ_{max} values observed in the alkylated benzenes, it was suggested that these data reflected a unique ground-state interaction between C_{60} and the arene.

In our experiments, we observed a red shift of 2 nm in the C_{60} bands at ~405 and ~490–630 nm as the solvent was changed from cyclohexane to benzene. Furthermore, this change in solvent seemed to broaden the latter bands slightly. It is important to note, however, that the magnitude of the cyclohexane/benzene solvent effect on the C_{60} absorption spectrum is extremely small in comparison with the phenomenon we report in Figs. 1 and 2. Specifically, the C_{60}–naphthalene data we report using a solvent of toluene do not change significantly if cyclohexane is used as the solvent. We chose to work in either toluene or benzene, as opposed to cyclohexane, because of the better solubility of C_{60} in the arene solvent [19].

We used the Drago–Rose modification of the Benesi–Hildebrand approach [20–23] to quantify the equilibrium constant K_{eq} for ground-state complex formation between C_{60} and MN in toluene. A 1:1 stoichiometry between C_{60} and MN was assumed. Absorption spectra were recorded from solutions in which (a) the C_{60} concentration was fixed at 1×10^{-4} M and (b) the MN concentration was varied over the range 0.32–6.4 M. The resultant Drago–Rose plots were characteristic of those observed for the formation of very weak or "contact" complexes [23,24]. This conclusion is supported by the small value of K_{eq} obtained from these plots (0.08 ± 0.02 M^{-1}) [2]. We did not observe an isosbestic point in the C_{60}–MN absorption spectra, which is likewise consistent with the interpretation of a ground-state complex that is not bound. The extinction coefficient ϵ for the C_{60}–MN cooperative transition obtained from the Drago–Rose analysis is $(1.1 \pm 0.2) \times 10^4$ M^{-1} cm^{-1} at 425 nm.

Caution must be exercised in relying too heavily on values of K_{eq} and ϵ obtained from a Drago–Rose analysis for weak complexes. At the least, it should be established that such values were obtained under experimental conditions in which the probability of binding or complex formation is appreciable. For our data in particular, the saturation fraction S of the dilute component exceeds the minimum quantity of ~0.2 desired by Deranleau [25] for accurate data only at MN concentrations in excess of ~3 M $\{S = K_{eq}[MN]/(1 + K_{eq}[MN])\}$. A less stringent requirement for accuracy was set forth by Person [26] in which, for our case, the MN concentration should at least exceed ~1.3 M (i.e. $\sim 0.1/K_{eq}$).

3.2. Emission spectra

With the hope that we might be able to observe a distinctive emission from a C_{60}–naphthalene complex, we recorded steady-state emission spectra from toluene solutions of C_{60} and C_{60} co-dissolved with MON. Upon excitation of both the C_{60} and C_{60}–MON solutions at wavelengths ranging from 355 to 532 nm, we observed the comparatively weak ~650–800 nm fluorescence [27,28] from C_{60} (Fig. 3). At wavelengths shorter than ~620 nm in the C_{60} solution, we also observed Raman scattered light derived from the solvent. In our spectra, this scattered light appeared with a tail that extended out to about 620 nm. As expected for Stokes scattering, this apparent emission shifted to longer wavelengths by an amount that equaled a corresponding red shift in the excitation wavelength. The C_{60} emission band shown in Fig. 3 did not shift with a change in excitation wavelength. In solutions containing a high concentration of MON, the intensity of Raman scattered light at wavelengths less than ~650 nm, although still weak, was nevertheless larger than that observed in the absence of MON. Because of the masking effects of such scattering subsequent to irradiation into the C_{60}–MON absorption band, we are hesitant to ascribe any

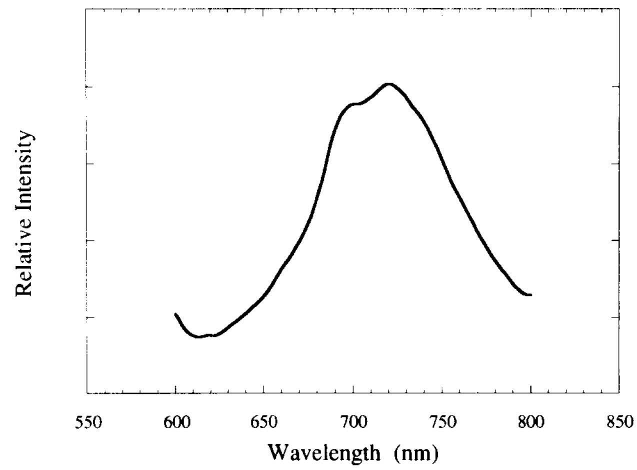


Fig. 3. Emission spectrum recorded over the range 600–800 nm subsequent to 500 nm excitation of C_{60} in toluene (λ_{max} = 720 nm).

---

[2] It should be noted that if a ground-state complex indeed exists between toluene and C_{60}, then our results likely underestimate the stability of the C_{60}–MN complex. The following equilibrium constants for ground-state complex formation, obtained from Benesi–Hildebrand studies, have been reported for the interaction between C_{60} and amines: C_{60}–*N*,*N*-dimethylaniline, 0.047 ± 0.010 M^{-1} in toluene [4]; C_{60}–triethylamine, 0.36 M^{-1} in benzene [6]; C_{60}–diphenylamine, 0.04 M^{-1} in benzene [6]; C_{60}–triphenylamine, 0.05 M^{-1} in benzene [6]; C_{60}–*N*,*N*-diethylaniline, 0.18 ± 0.04 M^{-1} in methylcyclohexane [5].

"emission" observed at ~500–650 nm to a C_{60}–MON exciplex.

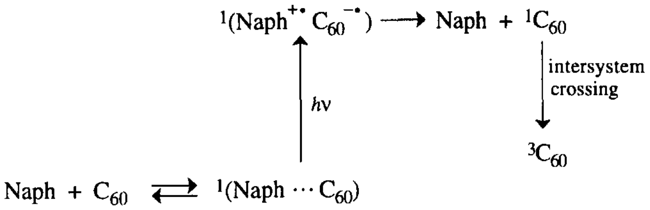
Solutions of C_{60} and C_{60} co-dissolved with MON were prepared such that the absorbances at 500 nm were identical. In the C_{60}–MON solution, where a large fraction of the incident light at 500 nm pumps the C_{60}–MON cooperative transition (Figs. 1 and 2), the intensity of the emission with λ_{max} at 720 nm was the same as that observed subsequent to excitation of the solution lacking MON[3]. These data indicate that the C_{60}–MON state initially populated by light absorption principally decays to yield the locally excited fluorescent state of C_{60}.

3.3. Flash absorption spectra

Upon 416 nm excitation, flash absorption spectra were recorded from toluene solutions of C_{60} and C_{60}–MN over the range 640–800 nm. For both solutions, a spectrum identical with that reported for the C_{60} triplet state [29–31] was recorded (λ_{max} ~740 nm; shoulder at ~670 nm). With reference to the discussion by Bensasson et al. [29], we obtained a ratio of absorbance values at 740 and 670 nm of 1:0.48. When optically matched solutions of C_{60} and C_{60}–MN were irradiated at 416 nm ($A_{416} = 0.40$), the triplet absorbance at 740 nm was essentially identical for both the C_{60} and C_{60}–MN solutions[4]. Because the quantum yield of C_{60} triplet is ~1 [32–34], it thus appears that the state initially populated by irradiation into the C_{60}–MN absorption band relaxes to form the localized triplet state of C_{60} with unit efficiency.

4. Conclusions

C_{60} forms a ground-state contact complex with naphthalenes that absorbs light to populate what appears to be an excited state with CT character. Although there is published precedent to indicate that singlet CT states can intersystem cross to populate directly a locally excited triplet state [35], our system behaves otherwise. Specifically, the C_{60}–naphthalene complex initially populated by light absorption decays to yield the locally excited fluorescent state of C_{60} which, in turn, is the precursor to the locally excited C_{60} triplet state (Scheme 1).



Scheme 1.

Acknowledgment

This work was supported by the National Science Foundation under Grant CHE-9402145. We thank Dr. Paul Cahill (Sandia National Laboratories) for a gift of C_{60}. We also thank Dr. Cahill, Professor C.S. Foote (UCLA) and Dr. R.V. Bensasson (CNRS, Paris) for helpful comments during the course of this work.

References

[1] R.D. Scurlock, S. Nonell, S.E. Braslavsky and P.R. Ogilby, *J. Phys. Chem., 99* (1995) 3521.
[2] S. Leach, M. Vervloet, A. Despres, E. Breheret, J.P. Hare, T.J. Dennis, H.W. Kroto, R. Taylor and D.R.M. Walton, *Chem. Phys., 160* (1992) 451.
[3] J.P. Hare, H.W. Kroto and R. Taylor, *Chem. Phys. Lett., 177* (1991) 394.
[4] R.J. Sension, A.Z. Szarka, G.R. Smith and R.M. Hochstrasser, *Chem. Phys. Lett., 185* (1991) 179.
[5] Y. Wang, *J. Phys. Chem., 96* (1992) 764.
[6] D.K. Palit, H.N. Ghosh, H. Pal, A.V. Sapre, J.P. Mittal, R. Seshadri and C.N.R. Rao, *Chem. Phys. Lett., 198* (1992) 113.
[7] R. Seshadri, C.N.R. Rao, H. Pal, T. Mukherjee and J.P. Mittal, *Chem. Phys. Lett., 205* (1993) 395.
[8] C.N.R. Rao, R. Seshadri, A. Govindaraj, J.P. Mittal, H. Pal and T. Mukherjee, *J. Mol. Struct., 300* (1993) 289.
[9] K.I. Priyadarsini, H. Mohan, A.K. Tyagi and J.P. Mittal, *Chem. Phys. Lett., 230* (1994) 317.
[10] M. Kristiansen, R.D. Scurlock, K.-K. Iu and P.R. Ogilby, *J. Phys. Chem., 95* (1991) 5190.
[11] R.D. Scurlock and P.R. Ogilby, *J. Phys. Chem., 93* (1989) 5493.
[12] S.L. Murov, I. Carmichael and G.L. Hug, *Handbook of Photochemistry,* Marcel Dekker, New York, 1993.
[13] D.R. Lide (ed.), *Handbook of Chemistry and Physics,* 74th edn., CRC Press, Boca Raton, FL, 1994.
[14] R.S. Mulliken and W.B. Person, *Molecular Complexes,* Wiley, New York, 1969.
[15] T. Pradeep, K.K. Singh, A.P.B. Sinha and D.E. Morris, *J. Chem. Soc., Chem. Commun.,* (1992) 1747.
[16] J.D. Crane, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.,* (1992) 1764.
[17] P.-M. Allemand, K.C. Khemani, A. Koch, F. Wudl, K. Holczer, S. Donovan, G. Gruner and J.D. Thompson, *Science, 253* (1991) 301.
[18] M.F. Meidine, P.B. Hitchcock, H.W. Kroto, R. Taylor and D.R.M. Walton, *J. Chem. Soc., Chem. Commun.,* (1992) 1534.
[19] R.S. Ruoff, D.S. Tse, R. Malhotra and D.C. Lorents, *J. Phys. Chem., 97* (1993) 3379.
[20] H.A. Benesi and J.H. Hildebrand, *J. Am. Chem. Soc., 71* (1949) 2703.
[21] N.J. Rose and R.S. Drago, *J. Am. Chem. Soc., 81* (1959) 6138.
[22] R.S. Drago and N.J. Rose, *J. Am. Chem. Soc., 81* (1959) 6141.
[23] T.J. Beugelsdijk and R.S. Drago, *J. Am. Chem. Soc., 97* (1975) 6466.

---

[3] Upon excitation of a C_{60}–MON solution at a wavelength where the CT state does not absorb (e.g. >600 nm), the emission intensity at 720 nm was the same as that observed upon excitation of a C_{60} solution lacking MON. These data indicate that MON does not significantly perturb C_{60} fluorescence.

[4] Upon excitation of a C_{60}–MN solution at a wavelength where only C_{60} absorbs, the resultant triplet absorbance at 740 nm was the same as that observed from a solution lacking MN. If the C_{60} triplet yield is independent of MN, then these data indicate that a high concentration of MN does not change the C_{60} triplet absorption coefficient.

[24] E.A. Gooding, K.R. Serak and P.R. Ogilby, *J. Phys. Chem.*, *95* (1991) 7868.

[25] D.A. Deranleau, *J. Am. Chem. Soc.*, *91* (1969) 4044.

[26] W.B. Person, *J. Am. Chem. Soc.*, *87* (1965) 167.

[27] D. Kim, M. Lee, Y.D. Suh and S.K. Kim, *J. Am. Chem. Soc.*, *114* (1992) 4429.

[28] S.P. Sibley, S.M. Argentine and A.H. Francis, *Chem. Phys. Lett.*, *188* (1992) 187.

[29] R.V. Bensasson, T. Hill, C. Lambert, E.J. Land, S. Leach and T.G. Truscott, *Chem. Phys. Lett.*, *201* (1993) 326.

[30] L. Biczok, H. Linschitz and R.I. Walter, *Chem. Phys. Lett.*, *195* (1992) 339.

[31] R.J. Sension, C.M. Phillips, A.Z. Szarka, W.J. Romanow, A.R. McGhie, J.P. McCauley, A.B. Smith and R.M. Hochstrasser, *J. Phys. Chem.*, *95* (1991) 6075.

[32] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz and R.L. Whetten, *J. Phys. Chem.*, *95* (1991) 11.

[33] R.R. Hung and J.J. Grabowski, *J. Phys. Chem.*, *95* (1991) 6073.

[34] M. Terazima, N. Hirota, H. Shinohara and Y. Saito, *J. Phys. Chem.*, *95* (1991) 9080.

[35] N. Mataga and M. Ottolenghi, in R. Foster (ed.), *Molecular Association, 2*, Academic Press, New York, 1979, pp. 1–78.

Note added in proof

Sibley et al. (*J. Phys. Chem.*, *99* (1995) 5274) recently reported discrete CT absorption bands for complexes of C_{60} with a variety of aromatic amines.