Inclusion complex of γ-cyclodextrin–C60: photophysical properties in the solid state using diffuse reflectance laser flash photolysis (DRLFP)

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Abstract

The transient behaviour of the solid γ-cyclodextrin–C60 complex was recorded by the diffuse reflectance laser flash photolysis (DRLFP) technique. The transient spectrum and kinetics of triplet decay are similar to those of the complex in aqueous solution, but there is a relevant absence of both triplet–triplet annihilation and molecular oxygen quenching processes.

Keywords: γ-cyclodextrin–C60 complex; Solid state; Photophysical properties; Diffuse reflectance laser-flash photolysis

1. Introduction

The photochemical and photophysical properties of C_{60} fullerene have been studied extensively in both organic solvents [1–4] and aqueous solution [5–8]. While pure C_{60} is soluble in a large number of organic solvents [9], its solubility in water is negligible and a 2 : 1 host : guest complex between γ-cyclodextrin and C_{60} was prepared [5–7] to obtain a water-soluble derivative. The photophysical properties [5,7] and electron transfer reactions [6] of the excited state of this complex in aqueous solutions have been reported, but at present there is no information on the photochemical behaviour in the solid state. The eventual application of C_{60} derivatives in the field of new materials science (e.g. as light limiters in laser-protecting glasses) requires clarification of their properties in the solid state [10]. We have shown that the photophysical properties of an insoluble polymeric equivalent of C_{60} [11] can be studied by the diffuse reflectance laser flash photolysis (DRLFP) technique [12]. In this paper, we report the interesting photophysical properties of the solid 2 : 1 host : guest complex between γ-cyclodextrin and C_{60} determined using the DRLFP technique.

2. Results and discussion

The complex (30 mg) was prepared from γ-cyclodextrin and fullerite (an Aldrich commercial mixture of C_{60} and C_{70}

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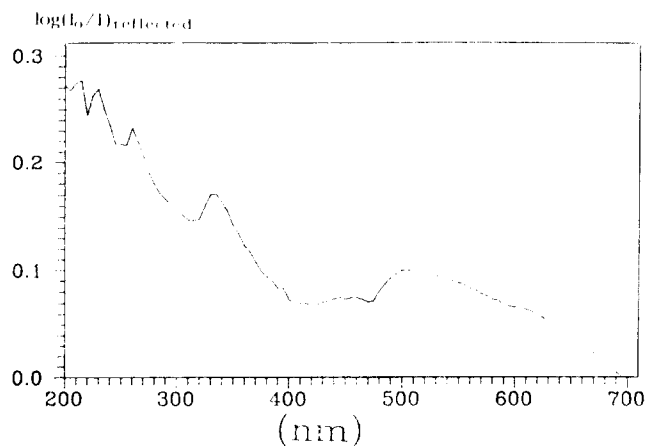
Fig. 1. Diffuse reflectance UV–visible ground state spectrum of the γ-cyclodextrin–C60 complex

fullerenes, 90 : 10) in methanol as described in Ref. [7]. It was studied using the diffuse reflectance accessory of an LKS.50 instrument (Applied Photophysics Ltd., UK). Fig. 1 shows the diffuse reflectance ground state spectrum of the complex. As expected, since it has been reported that C_{60}, but not C_{70}, can be complexed with γ-cyclodextrin, Fig. 1 shows the characteristic bands of C_{60} at 210, 260 and 330 nm, but not the characteristic bands of C_{70} [13]. The difference absorption spectrum recorded following 355 nm laser pulse (width, 9 ns; 68 mJ) excitation of an N_2-purged solid sample containing the γ-cyclodextrin–C_{60} complex is shown in Fig. 2. The maximum occurs at 740 nm and a typical decay is shown in the inset with a first-order fit. The deduced lifetime
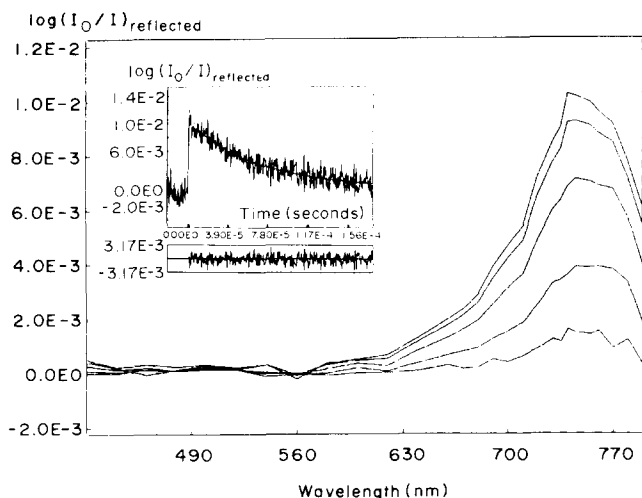
Fig. 2. Transient absorption spectrum of dry, nitrogen-purged, solid γ-cyclodextrin–C_{60} complex ($\lambda_{ex} = 355$ nm; intensity, 68 mJ per pulse; pulse width, 9 ns). From top to bottom: 2.4×10^{-6}, 9.6×10^{-6}, 30×10^{-6}, 80×10^{-6} and 180.0×10^{-6} s after the laser flash. Inset: decay traces and first-order fit at 740 nm.
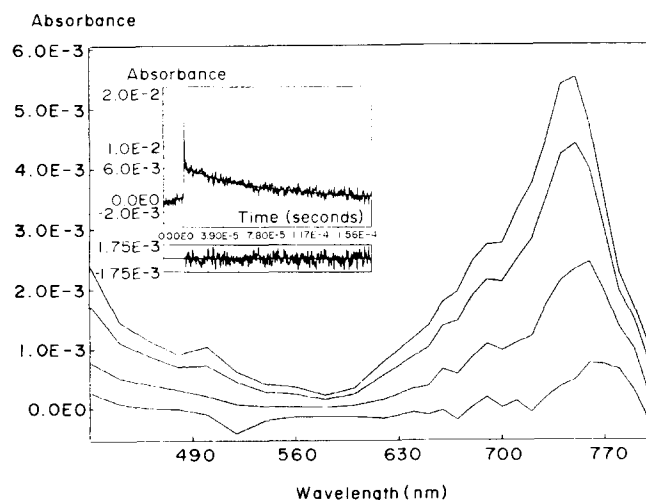

Fig. 3. Transient absorption spectrum of a nitrogen-purged aqueous solution of γ-cyclodextrin–C_{60} complex ($\lambda_{ex} = 355$ nm; intensity, 68 mJ per pulse; pulse width, 9 ns). From top to bottom: 2.4×10^{-6}, 9.6×10^{-6}, 30×10^{-6} and 80×10^{-6} s after the laser flash. Inset: decay traces and first-order fit at 740 nm.

is 69 ± 5 μs. Two points are worth noting: (1) the presence of air or pure oxygen does not affect the decay, indicating the absence of oxygen quenching; (2) the lifetime is not dependent on the laser energy; it remains constant although laser pulse energies as high as 98 mJ were used. This suggests the absence of triplet–triplet annihilation which is usually detected for excited C_{60} in solvents. For example, an aqueous solution of the γ-cyclodextrin–C_{60} complex shows the difference transient absorption spectrum displayed in Fig. 3. The maximum (whose shift to longer wavelengths as a function of decay has not yet been described) decays following two-component kinetics (see inset in Fig. 3) when the dissolved

sample is excited with the same laser pulse energy (68 mJ) as the solid complex: the fast component is attributed to the triplet–triplet annihilation process (60% of the decay) [5] (as the solubility of C_{60} in water is negligible [5,14], it seems unlikely that triplet–triplet annihilation could involve C_{60} molecules "free" in solution), while the slow component is attributed to the unimolecular triplet decay (deduced lifetime, 76 ± 5 μs; 83 μs [5]; 64 ± 5 μs [7]). The different behaviour of the 2 : 1 C_{60}–γ-cyclodextrin complex demonstrates that the two cyclodextrin units isolate the C_{60} molecule in the solid state preventing it from wasting energy in the triplet–triplet annihilation process as well as preventing photodecomposition by interaction wih molecular oxygen.

It can be concluded that the transient behaviour of the solid γ-cyclodextrin–C_{60} complex is similar to that described in aqueous solution both in the shape of the transient spectrum and in the kinetics of the triplet decay, but exhibits an absence of both the triplet–triplet annihilation and molecular oxygen quenching processes. These relevant differences are positive for the eventual application of this complex in the new materials area.

Acknowledgements

References

[1] T.W. Ebbesen, K. Tanigaki and S. Kuroshima, Chem. Phys. Lett., 181 (1991) 501.

[2] S. Nonell, J.H. Arbogast and C.S. Foote, J. Phys. Chem., 96 (1992) 4169.

[3] N.M. Dimitrijevic and P.V. Kamat, J. Phys. Chem., 96 (1992) 4811.

[4] D.K. Palit, A.V. Sapre, J.P. Mittal and C.N.R. Rao, Chem. Phys. Lett., 195 (1992) 1.

[5] T. Andersson, K. Nilsson, M. Sundahl, G. Westman and O. Wennerstroöm, J. Chem. Soc., Chem. Commun., (1992) 604.

[6] N.M. Dimitrijevic and P.V. Kamat, J. Phys. Chem., 97 (1993) 7623.

[7] K.I. Priyadarsini, H. Mohan, A.K. Tyagi and J.P. Mittal, J. Phys. Chem., 98 (1994) 4756.

[8] Z. Yoshida, H. Takekuma, S. Takekuma and Y. Matsubara, Angew. Chem. Int. Ed. Engl., 33 (1994) 1597.

[9] R.S. Ruoff, D.S. Tse, R. Malhotra and D.C. Lorents, J. Phys. Chem., 97 (1993) 3379.

[10] R.V. Bensasson, T. Hill, C. Lambert, E.J. Land, S. Leach and T.G. Truscott, Chem. Phys. Lett., 1201 (1993) 326.

[11] J.L. Bourdelande, J. Font and R. González-Moreno, J. Photochem. Photobiol. A: Chem., in press.

[12] F. Wilkinson and C.J. Willsher, Chem. Phys. Lett., 104 (1984) 272.

[13] H. Ajie, M.M. Alvarez, S.J. Anz, R.D. Beck, F. Diederich, K. Fostiropoulos, D.R. Huffman, W. Krätschmer, Y. Rubin, K.E. Schriver, D. Sensharma and R.L. Whetten, J. Phys. Chem., 94 (1990) 8630.

[14] R.S. Ruoff, D.S. Tse, R. Malhotra and D.C. Lorents, J. Phys. Chem., 97 (1993) 3379.