

# Inclusion complex of calix[8]arene-C<sub>60</sub>: photophysical properties and its behaviour as singlet molecular oxygen sensitiser in the solid state

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Received 10 February 1998; accepted 12 February 1998

## Abstract

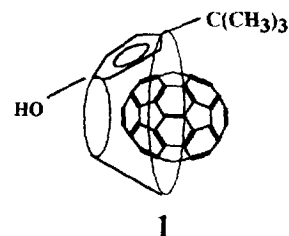
The inclusion complex calix[8]arene-C<sub>60</sub> has been studied in the solid state by means of nanosecond laser flash photolysis with diffuse reflectance (DRLFP) and NIR luminescence (TRNIR) detection techniques. The recorded transient absorption spectrum and its kinetics are similar to those showed by the inclusion complex of  $\gamma$ -cyclodextrin-C<sub>60</sub> in solid state. Contrarily, the new complex shows a very different behaviour against oxygen: the deduced deactivation quenching constant by molecular O<sub>2</sub> is  $k_q(\text{O}_2) = (1.1 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  in solid state, while the deactivation of triplet  $\gamma$ -cyclodextrin-C<sub>60</sub> by molecular O<sub>2</sub> in solid state had been reported as negligible. Consistent with this, TRNIR shows unequivocally that the solid calix[8]arene complex photosensitises the formation of singlet molecular oxygen, O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ), while the  $\gamma$ -cyclodextrin complex does not. O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ) has a lifetime of 16  $\mu\text{s}$  in the heterogeneous solid calix[8]arene complex-air system. Both complexes seem to show complementary properties to be used in the area of new materials. © 1998 Elsevier Science S.A. All rights reserved.

**Keywords:** Calix[8]arene; C<sub>60</sub>; Fullerene; Complex; Solid state; Transient behaviour; Singlet oxygen sensitiser

## 1. Introduction

Since fullerenes were discovered, many efforts have been devoted to clarify their properties [1–11]. The photophysical behaviour of C<sub>60</sub> in solution [8–11] is well known. Recently, the transient behaviour of pure C<sub>60</sub> [12] and other fullerene-derivatives [13,14] has also been studied in solid state by means of the diffuse reflectance laser flash photolysis (DRLFP) technique [15] or transmission laser flash photolysis [16]. The eventual application of these solid C<sub>60</sub> derivatives in the field of new material science is the reason for such efforts. The 2:1 host:guest inclusion complex of  $\gamma$ -cyclodextrin and C<sub>60</sub> is one of them [14]; its solid excited state (triplet) does not experience triplet-triplet annihilation nor deactivation by molecular oxygen; it has been suggested that the two cyclodextrin units isolate the C<sub>60</sub> molecule preventing it from wasting energy in the triplet-triplet annihilation process and from photodecomposition by interaction with molecular oxygen. As a consequence, this complex is an inefficient singlet oxygen sensitiser. In the field of new materials, however, it is useful to have available a good solid singlet oxygen sensitiser. Indeed, photosensitization of sin-

glet oxygen in heterogeneous gas-solid systems has been reported in the past [17–20], even from a C<sub>60</sub> film [21]. In this paper, we report our studies on the inclusion complex of calix[8]arene-C<sub>60</sub>, **1**, that shows a transient behaviour similar to the one described for  $\gamma$ -cyclodextrin-C<sub>60</sub> except for the occurrence of being efficiently deactivated by molecular oxygen, thus sensitising the formation of singlet molecular oxygen O<sub>2</sub>(<sup>1</sup> $\Delta_g$ ). Both complexes show, then, complementary properties to be used in the area of new materials.



## 2. Results and discussion

The 1:1 complex, **1**, was prepared from calix[8]arene and commercial C<sub>60</sub> (Acros Chemical, 99.9%) as described in

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Ref. [22]. Its diffuse reflectance ground state spectrum has been recorded using the diffuse reflectance accessory of an LKS50 instrument (Applied Photophysics, UK) and it is shown in Fig. 1. The spectrum is essentially the sum of the aromatic absorption of the calix[8]arene moiety and the characteristic bands of  $C_{60}$  (at 220 nm, 260 nm, 330 nm, and a broad band extending from 480 to 680 nm). In the 420–440 nm range, an additional shoulder can be observed resulting from the charge–transfer interaction between the electron-rich calixarene and the fullerene. The difference transient absorption spectrum of a  $N_2$ -purged solid powder sample has been recorded with the above-mentioned LKS50 spectrometer using a 532-nm laser pulse of a Q-switched Nd:YAG laser for excitation (Spectron Laser Systems, UK; width, 9 ns; 0.8 mJ/pulse). The spectrum, shown in Fig. 2, shows a single broad band centred at 780 nm. The transient absorption has a lifetime of  $1.7 \pm 0.2 \mu\text{s}$  (see the decay trace (a) in Fig. 3) and is assigned to the triplet of the solid  $C_{60}$  complex. The lifetime is very short compared to other solid samples (e.g.,  $40 \pm 5 \mu\text{s}$  for  $^3C_{60}$  covalently bound to insoluble crosslinked polystyrene [13];  $69 \pm 5 \mu\text{s}$  for the  $\gamma$ -cyclodextrin- $C_{60}$  complex [14];  $640 \pm 50 \mu\text{s}$  for solid  $C_{60}$  [12]). This is most likely a consequence of the charge–transfer interaction

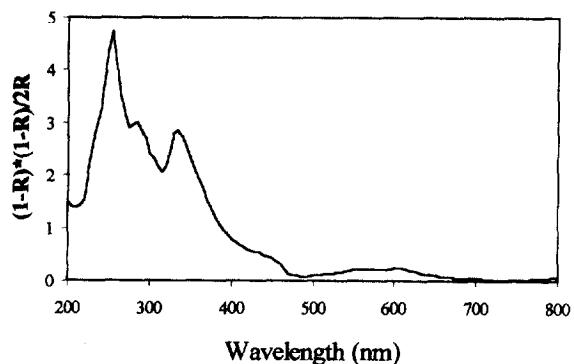


Fig. 1. Diffuse reflectance UV-Vis ground state spectrum of solid 1:1 calix[8]arene- $C_{60}$  complex.

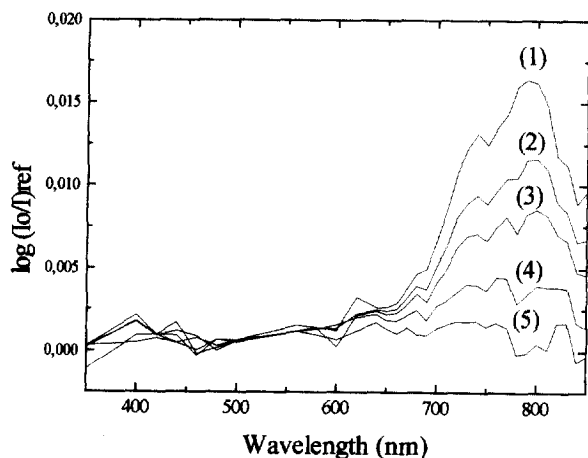


Fig. 2. Transient absorption spectrum of dry, nitrogen-purged solid 1:1 calix[8]arene- $C_{60}$  complex ( $\lambda_{ex} = 532 \text{ nm}$ , intensity 0.8 mJ/pulse, pulse width 9 ns). (1) 0.8, (2) 1.2, (3) 1.6, (4) 2.8 and (5) 18  $\mu\text{s}$  after laser flash.

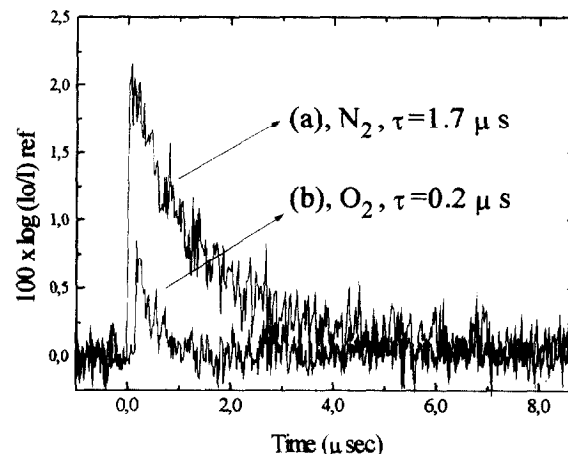


Fig. 3. Decay traces at 780 nm (conditions as in Fig. 2) in: (a)  $N_2$ -saturated, and (b)  $O_2$ -saturated solid 1:1 calix[8]arene- $C_{60}$  complex.

between the calixarene and the  $C_{60}$ . The lifetime and the shape of the transient absorption spectrum are independent of the laser energy in the range 0.8–30 mJ; this suggests a negligible contribution of the triplet–triplet annihilation process, thus preventing the energy waste of the excited complex.

Molecular oxygen deactivates the solid triplets of this 1:1 complex. We have followed the decay of the  $C_{60}$  triplet at 780 nm at different oxygen concentrations (see Fig. 3 for decays of  $N_2$ -purged (a) and oxygen-saturated (b) samples) and determined the rate constant for the quenching of the solid  $C_{60}$  triplet to be  $k_q(O_2) = (1.1 \pm 0.1) \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . This value is one order of magnitude larger than the deactivation constant observed for  $^3C_{60}$  covalently bound to insoluble crosslinked polystyrene,  $k_q(O_2) = (1.3 \pm 0.4) \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [13], and is slightly smaller than the one reported for a  $\gamma$ -cyclodextrin- $C_{60}$  complex in water solution,  $k_q(O_2) = 8.0 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  [23], but much larger than for the solid cyclodextrin- $C_{60}$  complex which is negligible [14]. The formation of  $O_2(^1\Delta_g)$  has been investigated, monitoring its characteristic phosphorescence at 1270 nm by means of a reversed bias germanium diode North Coast EO-817P [24]. The diode was placed at  $90^\circ$  to the excitation beam and at ca.  $60^\circ$  to the sample cuvette to prevent the reflected beam to impinge directly onto the diode surface. A series of filters were placed between cuvette and detector to attenuate the scattered laser light reaching the detector. In our hands, the best results were achieved using three cut-off filters at 555, 850 and 1050 nm followed by an interference filter at 1270 nm. In addition, a Schott KG5 filter was placed in the laser beam path to remove any residual IR component. Irradiation of the calix[8]arene- $C_{60}$  complex both under air and oxygen produced a transient luminescence whose decay could be fitted with two exponentials: a fast intense one with the decay time of the detector (ca. 350 ns) and a slow one with lifetime 16  $\mu\text{s}$  (Fig. 4). The latter disappeared when the sample was purged with nitrogen. Interestingly, it was also absent when the  $\gamma$ -cyclodextrin- $C_{60}$  complex was used instead of the calix[8]arene one, consistent with the lack of triplet quenching by oxygen in that system [14]. We con-

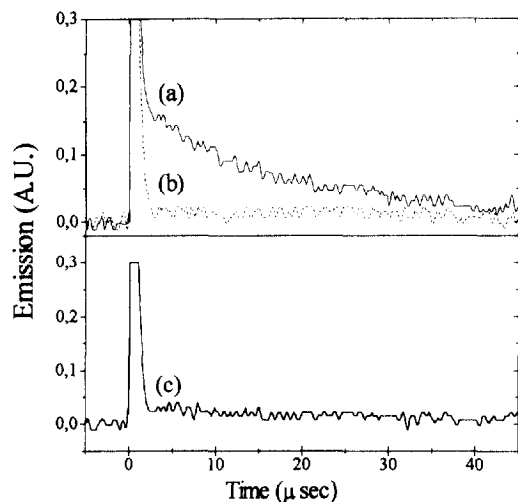


Fig. 4. Luminescence decay traces at 1270 nm: (a) air-saturated, and (b)  $N_2$ -saturated solid 1:1 calix[8]arene- $C_{60}$  complex. (c) Air-saturated solid 2:1  $\gamma$ -cyclodextrin- $C_{60}$  complex.

clude that  $O_2(^1\Delta_g)$  is formed by efficient energy transfer from the photoexcited fullerene complex to molecular oxygen in our solid calix[8]arene- $C_{60}$  powder system. This conclusion is in agreement with a previous report on singlet oxygen production by a  $C_{60}$  film [21].

The different behaviour of complex **1** and  $\gamma$ -cyclodextrin- $C_{60}$  in solid state is probably due to the different host:guest ratio in each complex: in the later two cyclodextrin units surround and protect the  $C_{60}$  moiety, while in the complex **1** only one calixarene unit surrounds the fullerene sphere leaving a larger part of its surface available to the molecular oxygen.

### 3. Conclusions

We have characterised the transient absorption behaviour of the inclusion complex calix[8]arene- $C_{60}$  in the solid state. Compared to the inclusion complex  $\gamma$ -cyclodextrin- $C_{60}$ , it shows a similar (triplet) absorption spectrum, a shorter lifetime, and it can be efficiently deactivated by molecular oxygen, being a good singlet oxygen sensitiser in solid state. Both complexes exhibit complementary properties that can be exploited in the area of new materials.

### Acknowledgements

Financial support from CIRIT (Generalitat de Catalunya) and DGCYT (Ministerio de Educación y Ciencia) (projects IN92-4363, PB92-0605 and QFN94-4613-C02-1) is gratefully acknowledged.

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