Optical limiting properties of soluble fullerene derivatives for incorporation in sol–gel materials

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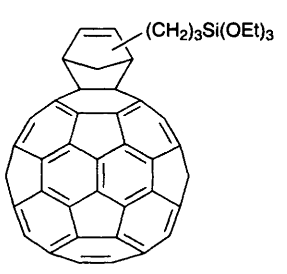
The optical limiting properties of fullerene derivatives containing silicon alkoxide functionalities are measured in toluene solution both at 532.0 and 652.0 nm and compare favourably with those of C_{60}.

While considerable effort has been successfully devoted to the study of the numerous physical and chemical properties of the fullerenes,[1] the design of fullerene-based devices is still an uncertain objective. However, in the continuing search for practical applications, the optical limiting (OL) properties exhibited by C_{60} and C_{70} occupy a leading position.[2] We have recently shown that C_{60} and C_{60} derivatives can be incorporated in thin silica matrices *via* sol–gel processing.[3] This methodology allows the deposition of transparent, optical-quality films on virtually any surface. Unlike polymeric substrates, sol–gel materials offer the advantage of good resistance against optical damage.[3,4] The presence of the fullerene dispersed in the glassy matrix would warrant the use of these films as shields against intense light pulses in a number of applications of, *e.g.* high-energy nanosecond lasers.

A major drawback in the incorporation of fullerenes in sol–gel matrices is their limited solubility in the polar organic solvents,[1] typically thf or ethanol, used in sol–gel processing.

With the aim of enhancing the solubility and to favour the covalent attachment to the silica matrix, we have prepared compounds **1** and **2a–d**.[5]† (Fig. 1).

In this paper we report the OL properties of toluene solutions containing compounds **1** and **2a–d** at 532 and 652 nm. In addition to the enhanced solubility, the results show that the OL properties of the new compounds are comparable with those of C_{60}.



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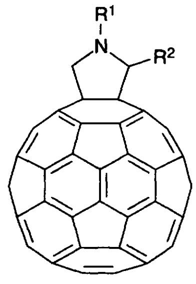

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2a $R^1 = -(CH_2)_3Si(OEt)_3$, $R^2 = -CO_2Me$
2b $R^1 = -(CH_2CH_2O)_3Me$, $R^2 = -(CH_2)_{10}S(OMe)_3$
2c $R^1 = -Me$, $R^2 = -(CH_2)_{10}Si(OMe)_3$
2d $R^1 = -Me$,

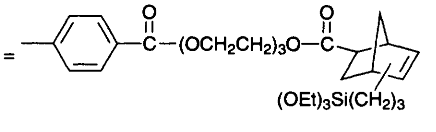
$R^2 =$ 

Fig. 1 C_{60} derivatives whose optical limiting properties have been investigated in this work

There is increasing consensus on the fact that the OL properties of the fullerenes are mainly due to the reverse saturable absorption (RSA) phenomenon.[6] For this to occur, it is required that the material exhibits spectral and photophysical properties allowing efficient optical pumping to an excited state. RSA is observed (instead of the well known saturable absorption of, *e.g.* organic dyes) if the excited state absorbs the pumping wavelength more strongly than the ground state. In the fullerenes the strongly absorbing excited state is the long-lived lowest triplet state (T_1) populated from the excited singlet state (S_1) with nearly unitary quantum efficiency.[7]

The UV–VIS spectra of the fused-ring C_{60} derivatives show that they retain electronic properties similar to those of C_{60}. A feature of the spectra relevant to their OL behaviour is the weak absorption extending over practically all the visible range. Compared to C_{60}, there are however several differences in the detailed structure of the visible absorption and a general tendency to exhibit lower absorption coefficients. The other known spectral and photophysical properties of the fused-ring C_{60} derivatives appear to be favourable to the RSA phenomenon. In particular, they exhibit a singlet–triplet quantum yield near unity and a triplet–triplet absorption peaked at *ca.* 700 nm with a molar absorption coefficient lower than that of the *ca.* 750 nm triplet–triplet absorption of C_{60}.[7]

In order to make all the data at a given wavelength directly comparable, OL measurements‡ were preformed in sequence on freshly prepared toluene solutions of C_{60} and of derivatives **1** and **2a–d** without modifying the laser alignment or other optical parameters which may affect the pulse profile and beam quality.

Fig. 2 compares the results obtained for toluene solutions of C_{60} and **1**. For both compounds, the linear transmission of the solutions was 72% at 532.0 nm and 87% at 652.0 nm. The data show similar nonlinear transmission properties although C_{60} has a better optical limiting performance in the green whereas **1** is superior in the red. Table 1 provides a summary of the OL data measured for the investigated compounds. For each solution, the linear transmittance [$T_0(\%)$] and the transmittance measured at a reference input fluence of 20 J cm^{-2} [$T_{20}(\%)$] are reported in the second and third column for the measurements at 532.0 nm and in the fifth and sixth column for those at 652.0 nm, respectively. The fourth and seventh columns report the values of the relative absorbance at 20 J cm^{-2} (A_{20}/A_0) which are > 1 when optical limiting is effective. Notice that, if RSA is responsible for the OL behaviour and if the laser fluence is above the saturation value at all points in the beam path inside the solution, A_{20}/A_0 approaches σ_E/σ_G, *i.e.* the ratio of the absorption cross section of the excited state (σ_E) to that of the ground state (σ_G).[8] Therefore, A_{20}/A_0 can be considered a good phenomenological parameter to qualify the properties of an OL material based on RSA. In the case of the present compounds and for laser pulses of the order of nanoseconds, σ_E refers to the lowest triplet state (σ_T). The data in Table 1 show that the OL behaviour of all the investigated derivatives is qualitatively similar to that illustrated in Fig. 2 for **1**, namely, their A_{20}/A_0 values at 532.0 nms are almost always comparable to that of C_{60}. At 652.0 nm all the fullerenes show improved OL behaviour with some derivatives exhibiting larger A_{20}/A_0 values than C_{60}. This is what one should expect if RSA is the dominant mechanism for OL. In fact the σ_T/σ_G ratio increases as the laser wavelength moves to the red and approaches the peak of the triplet–triplet absorption.[8] Whether the RSA of the derivatives is stronger than that of C_{60} depends on the balance between a closer peak wavelength of the triplet absorption at *ca.* 700 nm (instead of *ca.* 750 nm in C_{60}) and its lower molar absorption coefficient. Of course, differences in the ground-state absorption cross section may also play a role.

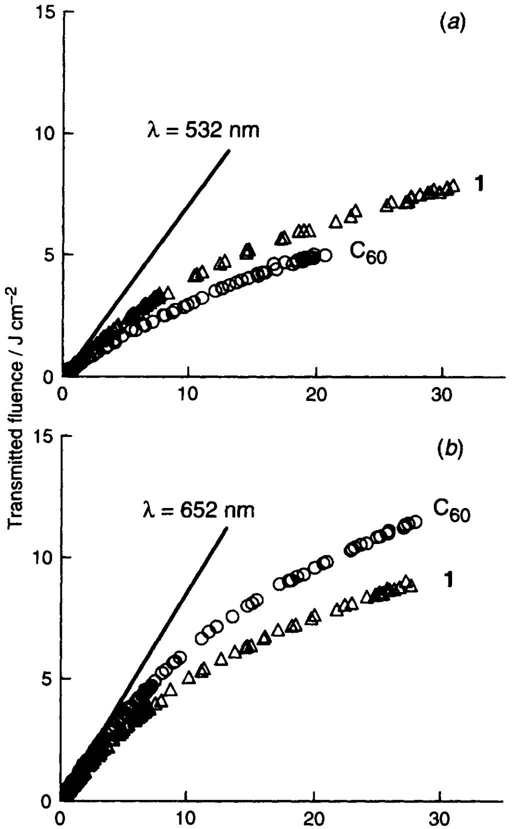


Fig. 2 Optical limiting data at 532 (*a*) and 652 nm (*b*) for C_{60} (○) and for **1** (△). The straight lines indicate the linear transmission of the solutions at low input fluence.

Table 1 Experimental values of transmittance at low fluence [T_0(%)], at 20 J cm^{-2} [T_{20}(%)] and relative absorbance (A_{20}/A_0) for C_{60} and for derivatives **1** and **2a–d** at 532 nm and at 652 nm

	532 nm			652 nm		
	T_0(%)	T_{20}(%)	A_{20}/A_0	T_0(%)	T_{20}(%)	A_{20}/A_0
C_{60}	72.0	24.9	4.23	86.5	48.7	4.96
1	72.0	30.0	3.66	87.0	38.7	6.82
2a	71.3	23.4	4.29			
2b	65.6	24.1	3.38			
2c	59.6	20.5	3.06	82.6	34.0	5.64
2d	50.0	22.1	2.18	86.8	52.7	4.52

We finally emphasize that, beside being endowed with potentially useful OL properties, the derivatives reported here exhibit solubilities in thf up to two orders of magnitude greater than that of C_{60} and possess functional groups enabling them to directly link to a silica network. Thin films and bulk samples have been prepared *via* the sol–gel method and show that highly homogeneous glasses with large fullerene concentrations can be obtained.[9]

The authors are grateful to Professor M. Guglielmi and Dr G. Brusatin for useful discussions. This work was developed in part within the 'Progetto Strategico Materiali Innovativi' of the Italian Consiglio Nazionale delle Ricerche.

Footnotes

† All new compounds exhibited correct analytical and spectroscopic data. The syntheses of compounds **1** and **2a–d** will be reported elsewhere.

‡ OL measurements were performed using an excimer pumped dye laser operating with Coumarin 503 (or Sulforhodamin B) and emitting 10 ns pulses at 532.0 (or 652.0) nm with 1 Hz repetition rate. The laser beam was focused onto the 10 mm sample cuvette using a lens with 200 mm focal length. The estimated beam waist was 50 μm in diameter. The incident and transmitted laser pulse energies were measured by using photodiodes calibrated against the signal from a surface absorbing calorimeter.

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Received, 15th May 1996; Com. 6/03467E