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A water soluble methanofullerene derivative: synthesis, micellar aggregation in aqueous solutions, and incorporation in sol–gel glasses for optical limiting applications

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Amphiphilic methanofullerene derivative **1** is water soluble and micellar aggregation has been evidenced by small-angle X-ray scattering measurements and UV/Vis spectroscopy. Thanks to the high solubility of **1** in polar solvents widely used in sol–gel processing, successful inclusion of **1** in the sol–gel could be easily achieved. The optical limiting properties of the doped sol–gel samples have been evaluated and a fast S_1–S_0 relaxation has been observed for these samples. This observation appears to be consistent with the presence of micellar aggregates of **1** in the sol–gel. Indeed, the interactions between the fullerene spheres of neighbouring molecules in the clusters may be at the origin of this fast S_1–S_0 relaxation as already shown in solid C_{60}-films.

Introduction

The development of optical power limiters with the aim of generating devices for the protection of human eyes or sensors against intense laser pulses of various wavelengths is a field of growing interest.[1] In contrast to ordinary neutral density filters, the transmission of an ideal optical limiting device drops rapidly as the incoming light intensity exceeds a certain threshold value.[2] Therefore a sensor placed behind such a device is protected against damage caused by strong laser irradiation, but its sensibility at low light intensities is not reduced as would be the case using an ordinary neutral density filter.[2] To achieve this intensity dependent transmission of the limiting device, different approaches are possible. Since much of the potential threat is caused by nanosecond laser sources, the transmission changes have to be very rapid. This excludes commercial photochromous glasses as used in ordinary eyeglasses, since their response time is too long.[2] Non-linear scattering and diffraction, two-photon absorption and reverse saturable absorption (RSA) are rapid physical phenomena more adequate for such a purpose.[2] RSA is often considered as one of the most interesting processes since it generally offers a low threshold of the energy density for the onset of the limiting action, very fast response times and the possibility of high transmission changes.[2] In reverse saturable absorbers, the transmission decrease is the result of an increasing absorption with increasing light intensity. The intensity dependent absorption of these materials originates from larger absorption cross sections of excited states compared to that of the ground state.[2] Such behaviour has been observed for buckminsterfullerene C_{60} over nearly the entire visible spectrum and several studies on C_{60} solutions have shown its great potential as an optical limiter.[3,4] However, for technical purposes, the use of a solid device is largely preferred due to its greater ease of handling as compared to liquid solutions. It has been shown that C_{60} keeps its limiting properties even after inclusion in solid matrices such as sol–gel glasses,[5] polymethyl methacrylate (PMMA) matrices[6] and glass–polymer composite samples.[7] As far as sol–gel glasses are considered, special procedures have to be employed since good solvents for fullerenes are incompatible with the sol–gel process.[5a,8a] The recent developments in the functionalization of fullerenes[9] allow the preparation of highly soluble C_{60} derivatives, and the electronic properties such as facile multiple reducibility,[10] optical non-linearity[8] or efficient photosensitization[11] that are characteristic of the parent fullerene are maintained for monofunctionalized C_{60} derivatives. As a part of this research, we now report the synthesis, incorporation in sol–gel matrices, and optical limiting properties of methanofullerene **1**.

Results and discussion

Synthesis and solution studies

The synthesis of methanofullerene **1** is depicted in Scheme 1. *tert*-Butyl ester **2** was obtained from 8-bromooctanoic acid (**3**) following the esterification conditions reported by S. W. Wright and co-workers.[12] This reaction is based on the treatment of carboxylic acid **3** with isobutylene generated *in situ* from the dehydration of *tert*-butyl alcohol in the presence of an acid catalyst. Thus, the treatment of **3** with *tert*-butyl alcohol in the presence of a dispersion of concentrated sulfuric acid on powdered anhydrous magnesium sulfate in CH_2Cl_2 at room temperature afforded *tert*-butyl ester **2** in 65% yield.

Treatment of **2** with 3,5-dihydroxybenzyl alcohol (**4**) and K_2CO_3 in DMF at 70 °C gave compound **5** in 52% yield. Malonate **6** was prepared in 66% yield from malonyl dichloride and **5** in CH_2Cl_2 in the presence of pyridine and 4-

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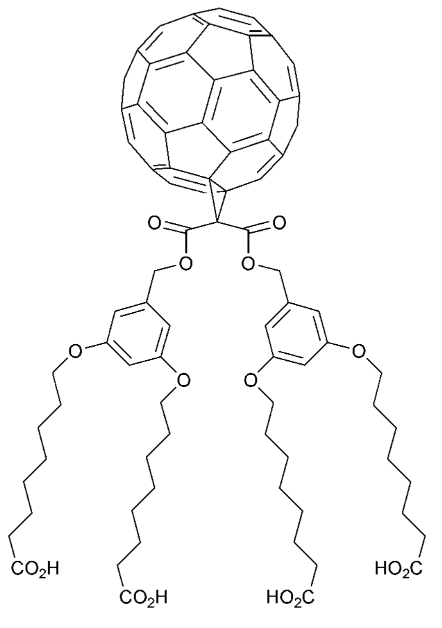

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dimethylaminopyridine (DMAP). The functionalization of C_{60} is based on the Bingel reaction.[13] Nucleophilic addition of a stabilized α-halocarbanion to the C_{60} core, followed by intramolecular nucleophilic substitution, leads to clean cyclopropanation of C_{60}. The α-halomalonate derivative is prepared *in situ* from the reaction of the malonate with iodine.[14] Treatment of C_{60} with **6**, iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene at room temperature afforded methanofullerene **7** in 37% yield. Selective cleavage of the *tert*-butyl esters[15] by treatment of **7** with trifluoroacetic acid in CH_2Cl_2 gave tetracarboxylic acid **1** in 84% yield. All spectroscopic data for **1** are in full agreement with the proposed formulation. Compound **1** is quite soluble in a wide range of solvents: chlorinated organic solvents (CH_2Cl_2, $CHCl_3$), THF, alcohols and water at slightly alkaline pH. Whereas the solubility has not been quantified, compound **1** is soluble to at least 5 mg ml^{-1} in all the above mentioned solvents. The UV/Vis spectrum of **1** in aqueous 0.1 M NaOH is broad when compared to the absorption spectrum of parent compound **7** (Fig. 1).

According to previously reported studies,[16] such a behaviour may arise from the amphiphilic character of **1** which may cause micellar aggregation in solution. The hydrophobic cores may,

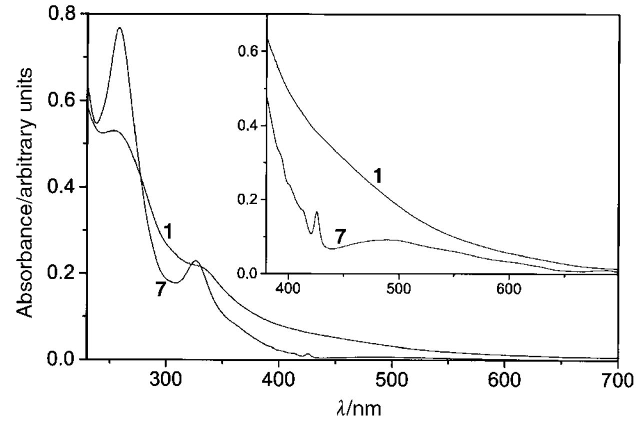
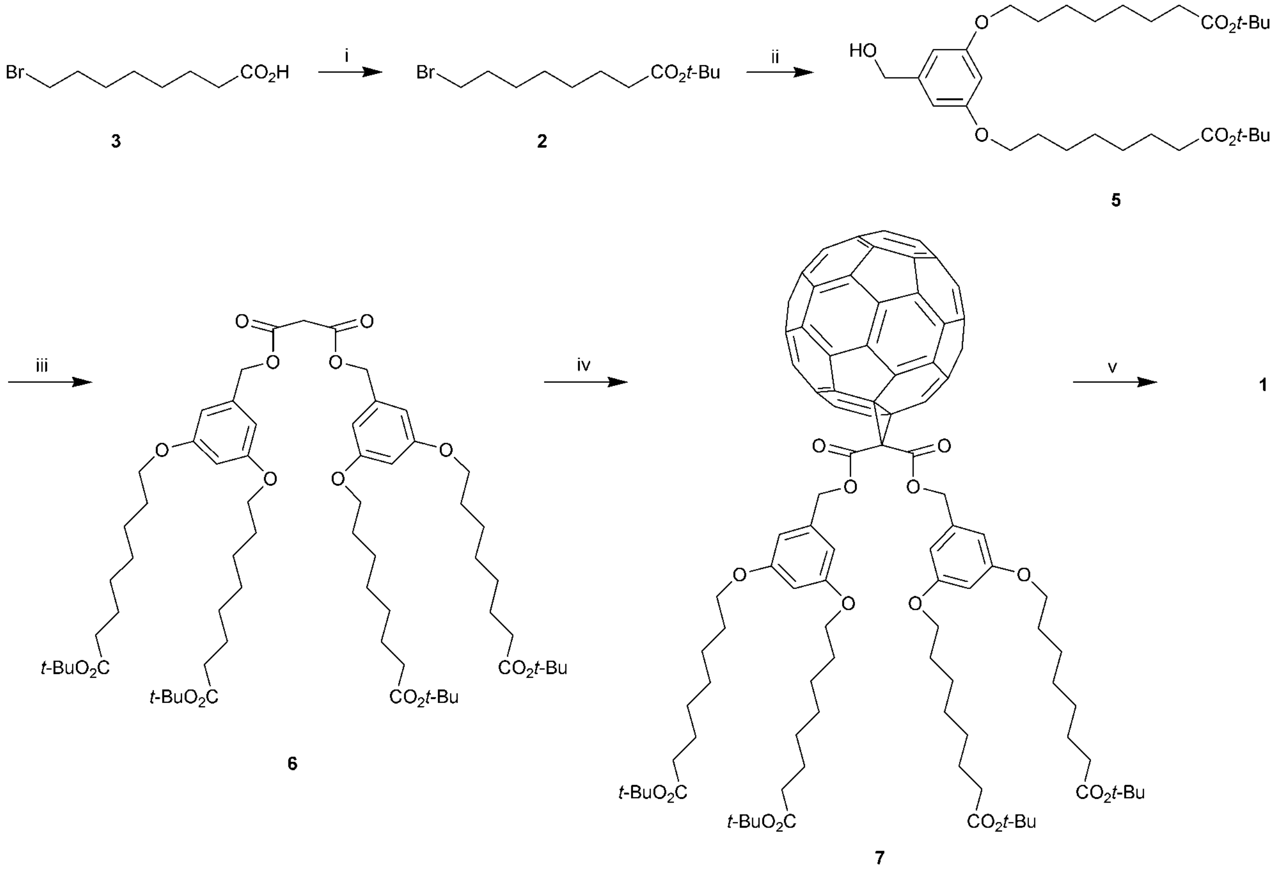


Fig. 1 UV/Vis spectrum of **1** in aqueous 0.1 M NaOH ($c = 5.5 \times 10^{-6}$ M) and of **7** in CH_2Cl_2 ($c = 6.5 \times 10^{-6}$ M). The inset shows the spectra obtained at higher concentrations (× 10).



Scheme 1 Preparation of compound **1**. *Reagents and conditions*: i) *t*-BuOH, H_2SO_4, $MgSO_4$, CH_2Cl_2, rt, 65%; ii) 3,5-dihydroxybenzyl alcohol (**4**), K_2CO_3, DMF, 70 °C, 52%; iii) malonyl dichloride, CH_2Cl_2, pyridine, DMAP, 0 °C to rt, 66%; iv) C_{60}, DBU, I_2, toluene, rt, 37%; v) CF_3CO_2H, CH_2Cl_2, rt, 84%.

in fact, form an actual cluster with the hydrophilic carboxy groups sticking out into the polar solvent. Clustering seems to prevail also in THF or alcohol solutions; the UV/Vis spectra obtained for THF or EtOH solutions of **1** are still broad. However, aggregation seems to be prevented upon further decrease in solvent polarity. In CH_2Cl_2 the ground state spectrum of **1** exhibits the same narrow and intense bands as unclustered **7**. The formation of aggregates of **1** in alkaline water were confirmed by small-angle X-ray scattering measurements. This experiment was performed on a 5% solution of methanofullerene **1** in aqueous 0.1 M NaOH. In the $\boldsymbol{q}$ range explored, the intensity of the X-ray scattering $I(\boldsymbol{q})$ is a monotonously decreasing function of the scattering vector $\boldsymbol{q}$. The absence of any peak reveals that no interactions between particles exist in the solution at this concentration. In the Guinier domain ($\boldsymbol{q}R < 1$), a radius of gyration R of about 20 Å is obtained from the slope of $\ln[I(\boldsymbol{q})]$ *vs.* $\boldsymbol{q}^2$, but the too weak intensity observed in the higher $\boldsymbol{q}$ range does not allow description of the shape of the particles. However, in the spherical micelles assumption, a micellar radius R_M of about 26 Å and a micellar volume V_M of about 75×10^3 Å^3 can be calculated. From the calculated molecular volume $V_m = 2.46 \times 10^3$ Å^3, an aggregation number N_M of about 30 molecules is deduced. Given the amphiphilic character of **1**, it is very likely that the micelles constitute clusters of C_{60} moieties surrounded by an aliphatic shell, with the solvated ions forming an ionic monolayer at the interface with the aqueous solvent.[17] The corresponding area per polar head S is about 70 Å^2, in good agreement with values found in micellar dispersions of sodium alkanoates.[18]

Incorporation in sol–gel glasses and optical limiting properties

Incorporation of fullerene derivative **1** was first attempted by soaking mesoporous silica glasses with a solution of compound **1**. The silica glasses were prepared by the sol–gel process as outlined in the Experimental section. The porous silica samples were soaked in a saturated THF solution of compound **1** or in a saturated chlorobenzene solution of C_{60}. After 30 minutes, the samples were removed from the solutions and dried at 40 °C for one hour. In the case of C_{60}, the resulting glass composites were dark brownish. In contrast, the samples obtained from the solution of **1** do not seem to be affected by the organic substance. In fact, these composites were colourless and no difference could be observed between the UV/Vis spectra of the initial glass and the soaked glass whatever the average size of porosity. Compound **1** seems to be unable to penetrate into the pores of the glass. This effect could be ascribed to the micellar aggregation of **1** in solution. The large size of the solvated assembly of molecules (diameter of *ca.* 5.2 nm for the non-solvated particles as determined by the small-angle X-ray scattering measurements) may prevent the penetration into the mesopores (maximum diameter: *ca.* 4.9 nm).

However, successful inclusion of compound **1** in the sol–gel could be achieved during the gelation process. A saturated solution of compound **1** in a 1 : 1 mixture of water and THF containing a small amount of ammonia was mixed quickly with the sol–gel preparation in the casting boxes. A few seconds after mixing, gelation occurred due to the pH change. The resulting dark red glasses were perfectly homogeneous and used as received for the optical measurements. The UV/Vis spectrum of a sol–gel glass is similar to that recorded in solution for compound **1**. This broad spectrum suggests that micellar aggregates of **1** are included in the glass.

The transmission of the sample at 532 nm and at room temperature as a function of the incoming laser fluence is shown in Fig. 2. With increasing pulse energy, the transmission of the sample clearly decreases. The threshold for the onset of the limiting action is located at about 3 mJ cm^{-2}, a value comparable or even slightly lower than that obtained with inclusions of C_{60} in sol–gel matrices.[5]

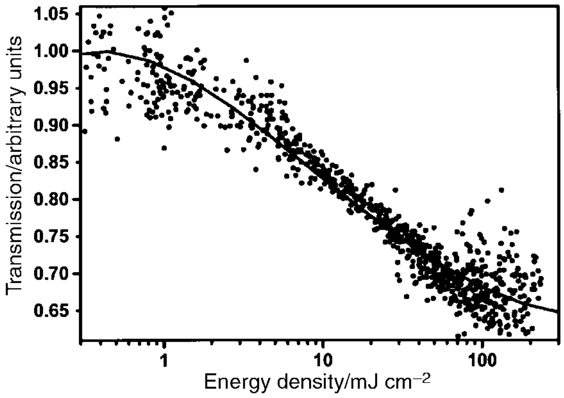


Fig. 2 Transmission *versus* incident fluence at 532 nm of a sol–gel sample containing compound **1**.

For the protection of the human eye, the unfocussed fluence at the eye must not exceed 1 μJ cm^{-2} per pulse. This means that our doped glasses can not be used for protection in simple eyeglasses, but they can only work efficiently if placed in an intermediate focal plane of an optical instrument such as binoculars. As the focalisation needs only to be mild, the insertion of such a material showing a low threshold for induced absorption should be easy.

The damage threshold of our samples is about 200 mJ cm^{-2}. Up to this fluence, the effect is fully reversible. This damage threshold is certainly determined by inhomogenities of the sol–gel sample (internal and/or at the surface) and could probably be considerably improved by polishing the surface and by optimising the drying process.

Time-resolved pump–probe experiments were performed in order to obtain information about the involved molecular states and their relaxation behaviour. Detailed knowledge of these properties is necessary for successful modelling and thereby optimisation of a limiting device.

In the pump–probe experiments, a powerful pump laser pulse creates an important excited state population. The transmission changes in the sample due to this excited state population are monitored by a weak probe pulse. In time delaying the probe pulse with respect to the pump pulse, the temporal evolution of the transmission and hence of the excited state population can be measured.

For isolated C_{60} molecules, the five-level-model of Fig. 3 is used to describe their reverse saturable absorption. C_{60} shows singlet and triplet electronic states, each electronic state giving rise to a manifold of associated vibronic states, shown by the thin lines above each bold line indicating the zero-vibration electronic state.

The dynamics following a photoexcitation of C_{60} in the visible region is as follows: the molecules excited by the pump

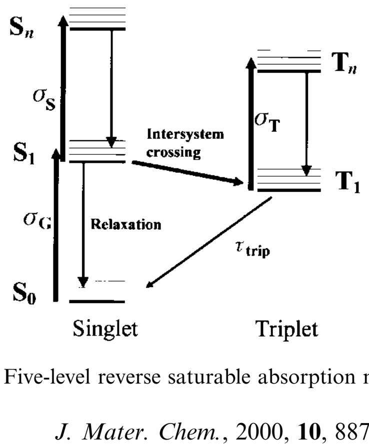


Fig. 3 Five-level reverse saturable absorption model.

pulse will relax rapidly from one of the vibronic substates of S_1 to the zero-vibration state of S_1. Then part of the excited molecules will relax directly to the S_0 ground state, the other part will undergo intersystem crossing to the metastable triplet state T_1. In C_{60}, both the S_1 and the T_1 states have considerably larger absorption cross sections than the ground state S_0 in the visible spectral region. Therefore, induced absorption can originate from either excited state population or from the molecules which have undergone intersytem crossing into the metastable triplet state. The latter gives rise to a long-lasting induced absorption.

The result of the time-resolved pump–probe experiment at 532 nm for a sol–gel sample doped with compound **1** is presented in Fig. 4. It shows the difference in the transmission of the sample either excited by the pump pulses or without excitation. The steep decrease in transmission shortly after the temporal coincidence of pump and probe pulses is due to the directly pump pulse induced singlet excited state population. This feature is followed by a slow re-increase in transmission, indicating a relaxation of this initially created population. It can be seen that this re-increase ends in a long-living plateau, indicating a very long-living excited state population, different from the initially created one but also capable of generating reverse saturable absorption. By analogy with C_{60} and due to the very long lifetime, the presence of the plateau can be attributed to the existence of an excited triplet state population.

A model of the observed dynamics yields a time constant of 490 ps for the depopulation of S_1 for **1** in the sol–gel, as compared to 1000–1200 ps for C_{60}[5a,19] or 1500–1700 ps for methanofullerenes[20] in solutions. The weaker triplet state-induced effect observed in our sample as compared to the singlet state-induced effect can originate from a low triplet quantum yield due to the interactions between the fullerene spheres of neighbouring molecules in the micellar aggregates. It has effectively been shown that in solid C_{60}-films, the triplet state is not noticeably populated due to fast S_1–S_0 relaxation resulting from the fullerene–fullerene interactions.[21]

Conclusions

Amphiphilic methanofullerene derivative **1** is a water soluble compound. Micellar aggregation has been evidenced by small-angle X-ray scattering measurements and UV/Vis spectroscopy. As a result, due to their large size, the solvated assembly of molecules is unable to penetrate mesoporous silica glasses. However, thanks to the high solubility of **1** in polar solvents, successful inclusion of **1** in the sol–gel could be easily achieved during the gelation process. The absorption spectrum of the resulting doped glasses suggests that micellar aggregates of **1** rather than isolated molecules are included in the glass. The optical limiting properties of the doped sol–gel samples have been evaluated and are comparable with the corresponding properties of C_{60}. A fast S_1–S_0 relaxation has been however observed for these samples. This observation appears to be consistent with the presence of micellar aggregates of **1** in the sol–gel. Indeed, the interactions between the fullerene spheres of neighbouring molecules in the clusters may be at the origin of this fast S_1–S_0 relaxation as already evidenced in solid C_{60}-films. Further studies are still under way in our laboratories in order to have a better insight about this issue.

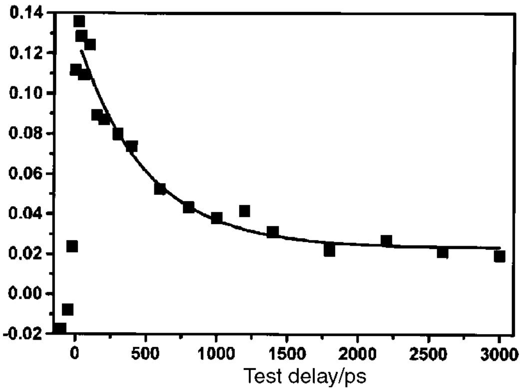


Fig. 4 Dynamics of induced decrease in transmission at 532 nm of a sol–gel sample containing compound **1**.

In conclusion, we have shown that the functionalisation of the fullerene sphere with hydrophilic addends leads to highly soluble derivatives that can be included in sol–gel matrices during the gelation process. The optical limiting properties of the resulting sol–gel glasses are similar to those of plain C_{60} in sol–gel glasses. However, the micellar aggregation of compound **1** is certainly at the origin of a fast S_1–S_0 relaxation and affects the optical limiting behavior of the sol–gel samples against nanosecond laser pulses. Further improvements could be expected by preventing the micellar aggregation. Work in this direction is currently under way in our laboratories.

Experimental

General methods

Reagents and solvents were purchased as reagent grade and used without further purification. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying *in vacuo* at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. Melting points were measured on an Electrothermal Digital Melting Point apparatus and are uncorrected. UV/Vis spectra (λ_{max} in nm (ε)) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 200 with solvent peaks as reference. FAB-mass spectra (*m*/*z*; % relative intensity) were taken on a ZA HF instrument with 4-nitrobenzyl alcohol as matrix. The scattering experiments were performed using an experimental device operating with linear collimation (infinite height slit conditions) of a monochromatic ($\lambda = 1.5405$ Å; CuKα1) X-ray beam. The scattered beams were recorded on a linear position sensitive counter in the scattering $\boldsymbol{q}$ vector ($4\pi/\lambda \times \sin\theta$ range between 0.06 and 3.5 $Å^{-1}$. The solution scattering curves were corrected by the subtraction of the background scattering from the solvent.

tert-Butyl 8-bromooctanoate (2)

H_2SO_4 (2.31 mL, 22.41 mmol) was added to a stirred suspension of anhydrous $MgSO_4$ (10.79 g, 89.63 mmol) in CH_2Cl_2 (150 mL) at room temperature. The resulting mixture was stirred for 15 min and **3** (5 g, 22.41 mmol) was added. The mixture was stoppered tightly and *t*-BuOH (10.51 mL, 112 mmol) was added with a syringe. After 18 h at room temperature, aqueous Na_2CO_3 was added and the resulting mixture was stirred until complete dissolution of $MgSO_4$. The aqueous layer was extracted twice with CH_2Cl_2; the combined organic layers were washed with water, dried ($MgSO_4$), filtered and concentrated. Rapid filtration on a silica plug (CH_2Cl_2) afforded 4.1 g of **2** (14.68 mmol, 65% yield). Pale yellow oil; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35–1.85 (m, 10 H), 1.44 (s, 9 H), 2.21 (t, $J = 7$ Hz, 2 H), 3.40 (t, $J = 7$ Hz, 2 H). ^{13}C-NMR ($CDCl_3$, 50 MHz): 24.87, 27.91, 28.03, 28.35, 28.77, 32.64, 33.78, 35.41, 79.84, 173.07; IR (CH_2Cl_2): 1722 cm^{-1} (C=O).

Compound 5

A solution of **2** (4 g, 14.32 mmol), **4** (942 mg, 6.82 mmol) and K_2CO_3 (3.95 g, 28.65 mmol) in DMF (80 mL) was heated to 70 °C for 20 h. The reaction mixture was then cooled to room temperature, filtered, and evaporated to dryness. The resulting dry residue was taken up in Et_2O–H_2O. After decantation, the organic layer was washed with brine (3 ×), dried ($MgSO_4$) and evaporated. Column chromatography (SiO_2, Et_2O–AcOEt 1 : 1) afforded 1.9 g (3.54 mmol, 52% yield) of **5**. Colourless glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35–1.85 (m, 21 H), 1.44 (s, 18 H), 2.21 (t, $J=7$ Hz, 4 H), 3.96 (t, $J=7$ Hz, 4 H), 4.61 (d, $J=6$ Hz, 2 H), 6.36 (t, $J=2$ Hz, 1 H), 6.49 (d, $J=2$ Hz, 2 H); ^{13}C-NMR ($CDCl_3$, 50 MHz): 14.02, 24.84, 25.74, 27.94, 28.85, 29.02, 35.38, 64.99, 67.74, 79.81, 100.21, 104.82, 143.32, 160.24, 173.16; $C_{31}H_{52}O_7$ (536.75): calcd C 69.4%, H 9.8%; found C 69.1%, H 10.0%.

Compound 6

Malonyl dichloride (210 mg, 1.49 mmol) was added to a stirred degassed solution of **5** (1.6 g, 2.98 mmol), pyridine (0.218 mL, 2.98 mmol) and DMAP (83 mg, 0.67 mmol) in CH_2Cl_2 (100 mL) at 0 °C. The solution was warmed slowly to room temperature (over 1 h) and stirred for 20 h. The resulting CH_2Cl_2 solution was washed with water, dried ($MgSO_4$), filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2–1% MeOH) yielded 1.13 g (0.99 mmol, 66% yield) of **6**. Colourless glassy product; ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35–1.76 (m, 40 H), 1.44 (s, 36 H), 2.21 (t, $J=7$ Hz, 8 H), 3.49 (s, 2 H), 3.91 (t, $J=7$ Hz, 8 H), 5.10 (s, 4 H), 6.39 (t, $J=2$ Hz, 2 H), 6.46 (d, $J=2$ Hz, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz): 24.82, 25.71, 27.92, 28.81, 28.86, 28.99, 35.34, 41.29, 66.98, 67.95, 79.68, 100.93, 106.12, 137.07, 160.24, 166.04, 173.00.

Compound 7

DBU (0.107 mL, 0.71 mmol) was added under argon to a stirred solution of C_{60} (207 mg, 0.286 mmol), I_2 (91 mg, 0.35 mmol) and **6** (360 mg, 0.315 mmol) in dry toluene (300 mL) at room temperature. After 6 h, the reaction mixture was filtered over a short plug of silica (toluene) and the solvent evaporated. Column chromatography (SiO_2, CH_2Cl_2–0.5% AcOEt) afforded 198 mg (0.11 mmol, 37% yield) of pure **7**. Dark red glassy product; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 258 (115 400), 326 (35 200), 425 (2330), 488 (1280), 685 nm (155); ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35–1.73 (m, 40 H), 1.43 (s, 36 H), 2.19 (t, $J=6$ Hz, 8 H), 3.87 (t, $J=6$ Hz, 8 H), 5.41 (s, 4 H), 6.38 (t, $J=2$ Hz, 2 H), 6.56 (d, $J=2$ Hz, 4 H); ^{13}C-NMR ($CDCl_3$, 50 MHz): 24.94, 25.90, 28.06, 28.96, 29.05, 29.15, 35.47, 51.78, 67.93, 68.79, 71.35, 79.84, 101.52, 106.83, 136.49, 138.92, 140.74, 141.76, 142.08, 142.85, 143.70, 144.37, 144.56, 144.78, 144.88, 145.04, 145.11, 160.36, 163.26, 173.11; IR (CH_2Cl_2): 1722 cm^{-1} (C=O); $C_{125}H_{102}O_{16}$ (1860.06): calcd C 80.7%, H 5.5%; found C 80.4%, H 5.7%.

Compound 1

A solution of **7** (365 mg, 0.196 mmol) and TFA (25 mL) in THF (100 mL) was stirred for 12 h at room temperature. The reaction mixture was concentrated and CH_2Cl_2 was added. The organic layer was washed with water until neutrality, dried ($MgSO_4$), filtered and evaporated to dryness. The resulting product was dissolved in a minimum of THF. Precipitation with hexane followed by filtration and drying under high vacuum yielded 270 mg (0.165 mmol, 84% yield) of **1**. Dark red solid (mp > 250 °C); UV/Vis (in aqueous 0.1 M NaOH): see Fig. 1; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 257 (95 000), 324 (27 500), 425 (3200), 488 (2200), 685 (130); ^{1}H-NMR ($CDCl_3$, 200 MHz): 1.35–1.73 (m, 40 H), 2.17 (t, $J=6$ Hz, 8 H), 3.87 (t, $J=6$ Hz, 8 H), 5.41 (s, 4 H), 6.39 (t, $J=2$ Hz, 2 H), 6.58 (d, $J=2$ Hz, 4 H); FAB-MS: 1635.7 (10%, $[M+H]^+$, calcd for $C_{109}H_{71}O_{16}$: 1635.5), 720.2 (100%, $[C_{60}]^+$, calcd for C_{60}: 720.0).

Mesoporous silica glasses

A solution of tetramethoxysilane (TMOS) in MeOH was added to a mixture of water, MeOH, nitric acid and formamide, the final composition of TMOS–MeOH–H_2O–$CHONH_2$–HNO_3 was 1 : 10 : 5 : 1 : 0.063 (molar ratio).[22] The reaction was followed by FTIR which showed that full hydrolysis of TMOS was reached in a few seconds. Then the condensation reaction took place and gelation occurred within 2 to 3 h depending on the temperature stated (normally at 40 °C). The gels were cast in small PMMA round boxes (diameter: 25 mm, height: 8 mm) and dried at 40 °C in a drying oven for 2 days. At this step a large shrinkage occurred leading to pieces of transparent xerogels of 10 mm in diameter and 0.4 mm in height. These xerogel pieces were further heat treated at 500–600 °C. These samples are mesoporous as shown by physisorption measurement. The mean pore diameter is 3.46 nm and the maximum pore diameter is 4.9 nm with a porous volume of 0.2133 cm^3 g^{-1}. The soaking experiments with this mesoporous glass substrates have been carried out as described in the text.

Inclusion of compound 1 in the sol–gel during the gelation process

A solution of **1** (12 mg mL^{-1}) in a 1 : 1 THF–H_2O mixture (2 mL) containing two drops of ammonia was added quickly to a sol–gel preparation (same components in the same ratio as described in the previous section) in the casting boxes. A few seconds after mixing, gelation occurred due to the pH change. At this step, compound **1** is included in the gel–glass. The samples were dried at 40 °C in a drying oven for 2 days. No further heating has been carried out on these samples and they were used as received for the optical measurements.

Optical measurements

To study the optical limiting properties, we measure the transmission of our doped glass samples as a function of the incoming fluence at room temperature. We use a frequency-doubled (active/passive mode locked) Nd : YAG laser at 532 nm with a pulse duration of 30 ps and a repetition rate of 5 Hz. At this wavelength, the linear transmission of the sample is about 60%. This linear transmission is caused by the inherent absorption of the active molecules by diffusion losses due to inhomogeneities of the sample. To take into account the intensity fluctuations of the laser source, a reference beam created by a beam splitter from the same laser beam as the excitation branch was used. The exciting pulses are focussed onto the sample by a lens of $f=16$ cm into a spot of 6400 μm^2. The transmitted light of the measurement pulses as well as that of the reference pulses is sent onto the same optical multichannel analyser. The incident intensity at the sample position is changed by means of calibrated neutral density filters.

Dynamics of reverse saturable absorption

The laser source is the same ps Nd : YAG laser as outlined above. Reference, pump and probe pulses are created from the same laser beam by beam splitters. The transmitted test pulses and the reference pulses are sent onto the same optical multichannel analyser. We use a half-wavelength plate and polarisers to achieve crossed linear polarisation between pump and probe pulses. Coherent effects are therefore largely suppressed and we observe exclusively the population dynamics. Furthermore, the crossed polarisation is used together with an analyser before the optical multichannel analyser in order to suppress stray light from the strong pump pulses. A discrimination system is used which ensures that only laser pulses within a certain energy window are accumulated.

Each measured point is the result of an accumulation of 200 laser pulses inside the energy window. By this means, energy fluctuations of the laser source can be largely suppressed.

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