Fullerodendrimers with peripheral triethyleneglycol chains: synthesis, mass spectrometric characterization, and photophysical properties

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Poly(aryl ether) dendritic branches terminated with peripheral triethyleneglycol chains have been attached to C_{60}. The resulting fullerodendrimers have been characterised by electrospray mass spectrometry (ESMS), which appears to be a particularly interesting analytical tool for the unambiguous structural assignment of such high molecular weight fullerene derivatives. Their photophysical properties have been systematically investigated in three solvents, namely toluene, dichloromethane, and acetonitrile. The changes observed in the photophysical properties along the series suggest an increasing interaction between the poly(aryl ether) dendritic wedges and the fullerene core, which brings about an increasing isolation of the central chromophore from the exterior. Finally, thanks to their high solubility, fullerodendrimers **1**–**4** have been easily incorporated in mesoporous silica glasses and preliminary measurements on the resulting doped samples have revealed efficient optical limiting properties.

Following the development of efficient synthetic procedures for the preparation of monodispersed cascade molecules, the design of functional dendrimers is more and more emphasized today.[1–3] In particular, the ability of a dendritic shell to encapsulate a functional core moiety and to create a specific site-isolated microenvironment capable of affecting the molecular properties has been explored in recent years.[3] A variety of experimental techniques has been employed to evidence the shielding of the core moiety and to ascertain the effect of the dendritic shell.[3] Among them, UV-Vis absorption and emission spectroscopy has proven to be very helpful since specific changes in the microenvironment of chromophoric cores can be monitored by observing changes in the intensity, shape, or position of absorption and luminescence bands.[4] On the other hand, the bimolecular deactivation of excited states resulting from the penetration of external quenchers through the dendritic shell allows for an evaluation of the accessibility of the core.[5] Despite the fact that in recent years C_{60} has become a widely employed building block in dendrimer chemistry,[6–9] studies aiming at evidencing dendritic effects on the photophysical properties of a fullerene core have never been reported. In this paper, we describe the ground state and excited state properties as well as the singlet oxygen sensitization of fullerodendrimers **1**–**4**[10] in different solvents. The changes of the photophysical properties observed along the series suggest an increasing interaction between the dendritic wedges and the central core, which brings about an increasing isolation of the central chromophore from the exterior. Finally, thanks to their high solubility, fullerodendrimers **1**–**4** have been easily incorporated in mesoporous silica glasses and preliminary measurements on the resulting doped samples have revealed efficient optical limiting properties.

Results and discussion

Synthesis

The synthesis of fullerene-functionalized dendrimers is currently an area of considerable interest.[6] Dendrimers with a C_{60} core,[7] peripheral C_{60} subunits[8] or a C_{60} sphere at each branching unit[9] have already been described. As far as fullerodendrimers with C_{60}-type cores are concerned, it should be noted that the functionalization of the fullerene sphere with dendritic branches dramatically improves the solubility of C_{60}. In the design of fullerodendrimers **1**–**4**, it was decided to attach poly(aryl ether) dendritic branches terminated with peripheral triethyleneglycol chains to obtain compounds soluble in a wide range of solvents. The dendritic branches **5**–**8** have been prepared as previously described[11] and MnO_2 oxidation afforded the corresponding aldehydes **9**–**12** (Scheme 1). The synthetic approach to prepare compounds **1**–**4** relies upon the 1,3-dipolar cycloaddition of the dendritic azomethine ylides generated *in situ* from the corresponding aldehydes and *N*-methylglycine. This methodology has proven to be a powerful procedure for the functionalization of C_{60} due to its versatility and the ready availability of the starting materials.[12] Thus, reaction of aldehydes **9**–**12** with *N*-methylglycine and C_{60} in refluxing toluene gave the corresponding fulleropyrrolidines **1**–**4** in 37 to 44% isolated yield after column chromatography on silica gel followed by gel permeation chromatography.

The stucture of fullerodendrimers **1**–**4** was confirmed by analytical and spectroscopic data. The ^{1}H-NMR spectra of **1**–**4** recorded in $CDCl_3$ exhibit the expected features with the signals arising from the poly(aryl ether) dendritic branches,

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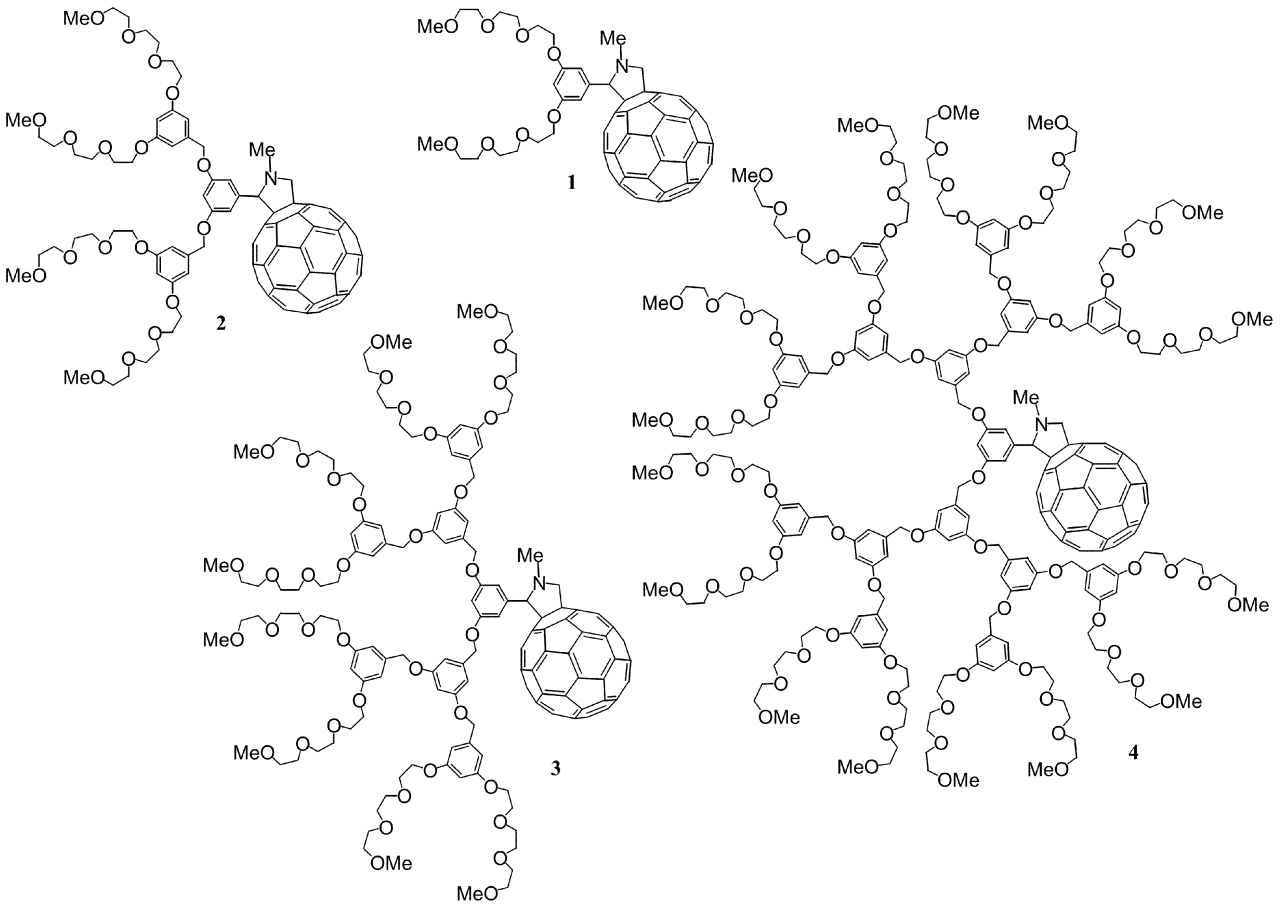


an AB quartet and a singlet for the pyrrolidine protons as well as a singlet for the N–CH_3 group. It is also important to note that the signals corresponding to the protons of the phenyl group directly attached to the pyrrolidine ring are broad at room temperature. As previously described for phenylfulleropyrrolidine derivatives,[13] this indicates restricted rotation of the phenyl substituent on the pyrrolidine ring. This was confirmed by variable-temperature NMR studies showing a clear coalescence at *ca.* 10 °C in all the cases and a reversible narrowing was observed in the spectra of **1**–**4**. The associated free energy of activation for the rotation of the phenyl group on the pyrrolidine ring was estimated by following the coalescence of the aromatic C–H and found to be similar ($\Delta G^{\ddagger} = 13$ kcal mol^{-1}) for the four compounds. The ^{13}C-NMR spectra of **1**–**4** were also in full agreement with their C_1 symmetry resulting from the presence of the asymmetric C atom in the pyrrolidine ring.

Mass spectrometry

An unequivocal structural analysis of compounds **1**–**4** requires also their mass spectrometric analysis. Indeed, several ionization techniques have been used successfully for the characterization of low molecular weight fullerene derivatives; electron impact (EI),[14] matrix-assisted laser desorption/ionization (MALDI)[15] or fast-atom bombardment (FAB).[16] However, for functionalized fullerenes of high molecular weight, these mass spectrometric methods are difficult to handle (and/or inefficient) and most often accompanied by high levels of fragmentation. Therefore, we propose here the use of electrospray mass spectrometry (ESMS) as an alternative. Indeed, ESMS is particularly suitable for large compounds[17] and the gentle nature of the ES process yields usually a simple mass pattern without fragments. In addition, we have already described a fruitful ESMS strategy to detect neutral high molecular weight functionalized fullerenes by taking advantage of their electrochemical properties.[9b] In the present case, ionization (by protonation) and therefore detection of the compounds was possible owing to the presence of the amine function and the addition of 1% formic acid in the solvent (CH_2Cl_2).

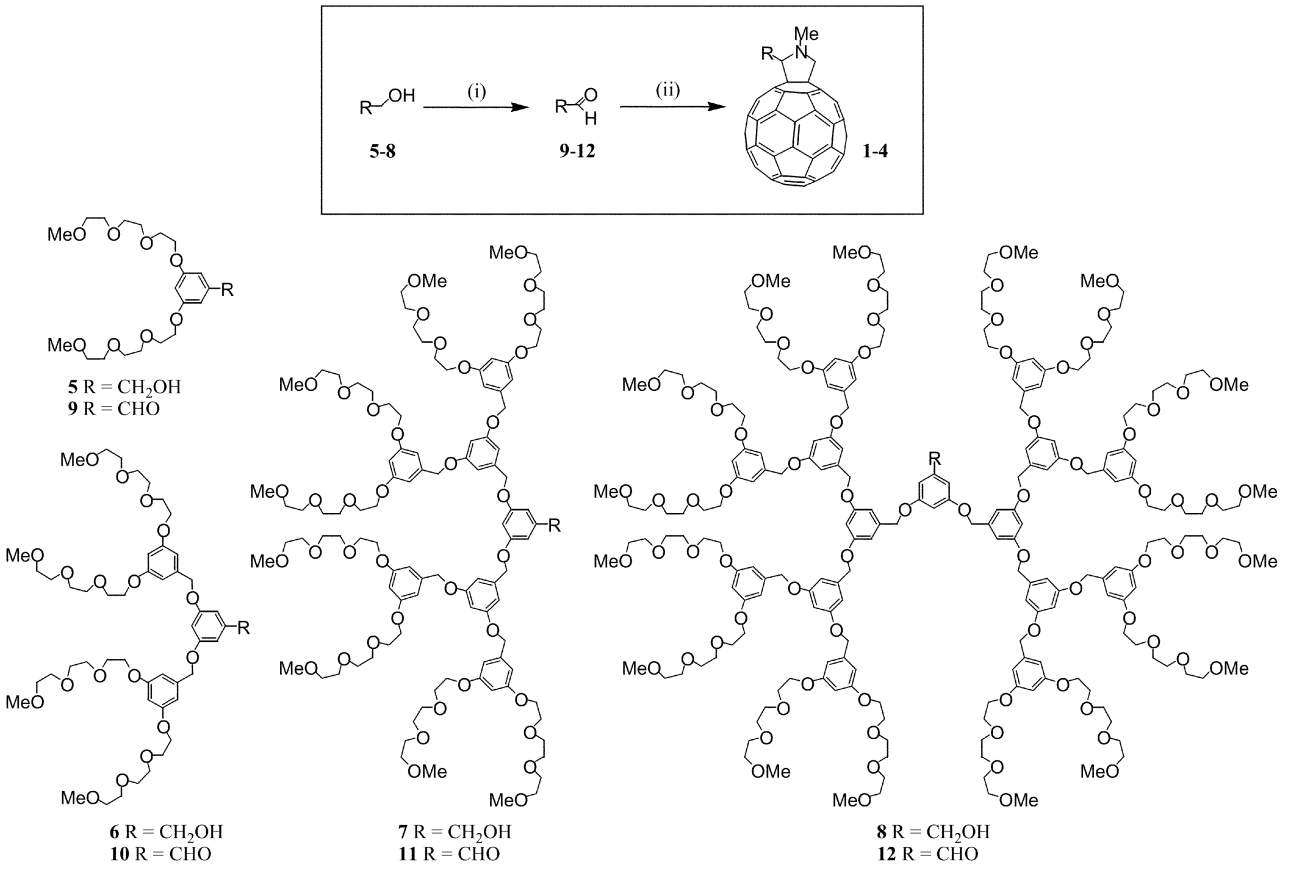
The ES mass spectra of **1** and **2** obtained in the positive mode are depicted in Fig. 1. In each case, only the expected singly charged ion resulting from the protonation of the compound is observed: at $m/z = 1179.2$ for $[\mathbf{1}+H]^+$ (calcd $m/z = 1179.2$) and at $m/z = 1715.9$ for $[\mathbf{2}+H]^+$ (calcd $m/z = 1715.9$). The isotopic pattern of the two observed peaks corresponds to the theoretical one, confirming the charge state of the ions.

The ES mass spectra of **3** (not represented here) and **4** (Fig. 2) recorded under the same conditions also show the presence of one singly charged peak corresponding to the expected protonated compound at $m/z = 2789.1$ (calcd m/z for $[\mathbf{3}+H]^+ = 2789.1$) and at $m/z = 4935.0$ (calcd m/z for $[\mathbf{4}+H^+]^+ = 4935.5$).

Photophysical studies

The electronic absorption spectra of **1**–**4** in toluene, dichloromethane, and acetonitrile (hereafter indicated as, respectively, $PhCH_3$, CH_2Cl_2, and CH_3CN) are reported in Fig. 3–5.

Fullerodendrimers **2**–**4** are sticky glassy compounds at room temperature, making precise weighting difficult; thus an accurate experimental determination of their molar extinction coefficients (ε) was not possible. The spectrum in ε units was experimentally determined only for **1** in CH_2Cl_2, in all the other cases the values reported are estimated by assuming the same molar extinction coefficient at 520 nm (1100 M^{-1} cm^{-1}). This can be considered a reasonable approximation in view of (*i*) the invariance of the C_{60} chromophoric unit along the series; (*ii*) the similar spectral shape for the various



Scheme 1 Preparation of compounds **1**–**4**. Reagents and conditions: (*i*) MnO_2, CH_2Cl_2, room temperature; (*ii*) C_{60}, *N*-methylglycine, toluene, Δ.

dendrimers above 500 nm; (*iii*) the little or no dependence of fullerene ε values on solvent polarity.[18]

The absorption spectra in CH_2Cl_2 and CH_3CN reveal the increasing contribution of the poly(aryl ether) dendritic branches above 250 nm and around 280 nm (shoulder) in passing from **1** to **4** (Fig. 4 and 5), in agreement with the dendrimers' structures. In all solvents changes of the absorption spectral shapes are observed for **1**–**4**. In particular we note: (*i*) an intensity decrease of the fullerene bands in the 250–350 nm region, quite remarkable for **4** and (*ii*) a progressive loss of spectral resolution in the visible region, particularly evident from the marked intensity reduction of the diagnostic fulleropyrrolidine absorption peaks at 431 and 706 nm. This might reflect a modification of the C_{60} chromophore solvation environment as a consequence of a tighter contact with the external dendritic arms containing aromatic units,[5e] possibly promoted by favourable electronic donor-acceptor interactions.[19] To bring some support to this hypothesis we note that the above effect (*ii*) is the strongest in polar CH_3CN (Fig. 5), where intramolecular stacking between the dendritic wedges and the hydrophobic central core is expected to be particularly effective.

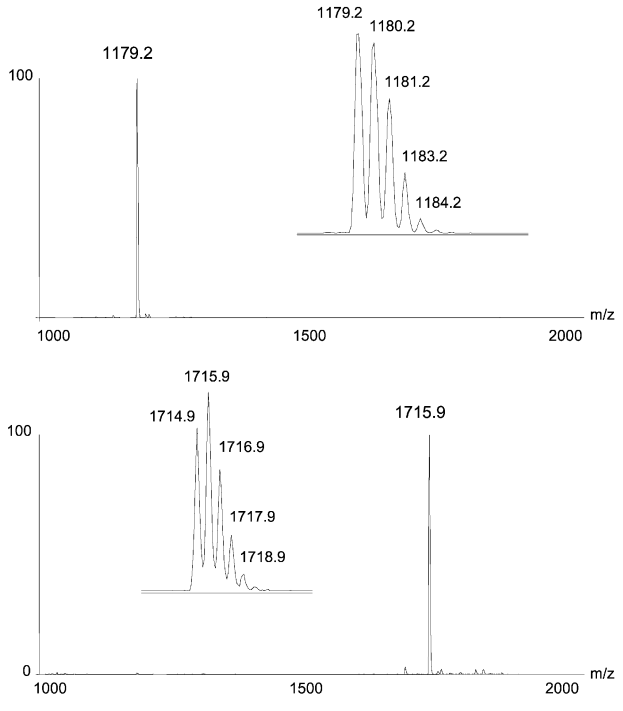


Fig. 1 ES mass spectrum of **1** (top) and **2** (bottom) and isotopic patterns observed for the two singly charged ions. Isotopic peaks are separated by 1 m/z unit.

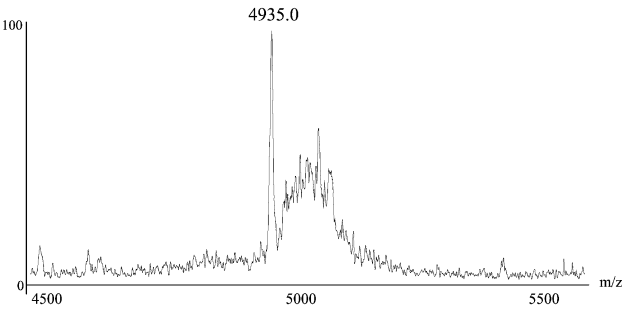


Fig. 2 ES mass spectrum of 3 recorded at $V_c = 160$ V; in this case the resolution capability of the quadrupole analyser ($R = 1000$) is not sufficient to obtain the isotopic pattern of the peak.

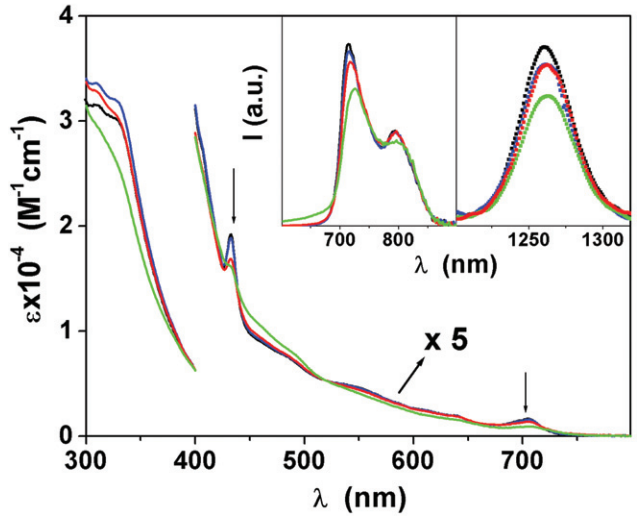


Fig. 3 Absorption spectra of **1**–**4** in toluene solution at 298 K; above 400 nm a scaling factor of 5 is applied. Inset: fluorescence (left, λ_{exc} = 370 nm, O. D. = 0.30) and sensitised singlet oxygen luminescence spectra (right, λ_{exc} = 480 nm, O. D. = 0.20) of **1**–**4**. **1** (black), **2** (blue), **3** (red), **4** (green). The ε values are estimated according to the procedure described in the text.

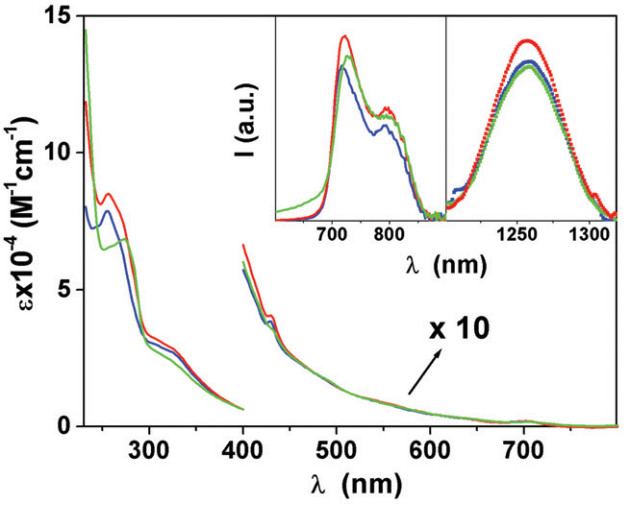


Fig. 5 Absorption spectra of **2**–**4** in CH_3CN solution at 298 K; above 400 nm a scaling factor of 10 is applied. Inset: fluorescence (left, λ_{exc} = 370 nm, O. D. = 0.30) and sensitised singlet oxygen luminescence spectra (right, λ_{exc} = 480 nm, O. D. = 0.20) of **2**–**4**. **2** (blue), **3** (red), **4** (green). **1** is not soluble in this solvent. The ε values are estimated according to the procedure described in the text.

The fluorescence spectra of **1**–**4** in the three solvents are also shown in Fig. 3–5, and a summary of luminescence data is reported in Table 1.

As a function of dendrimer size one can note: (*i*) a steady red-shift of the band maxima (up to 10–15 nm) in all solvents and (*ii*) a prolongation of the singlet lifetime for the largest dendrimer **4**, safely above the experimental uncertainty. These trends could be the consequence of changes in the dendrimers solvation environment, as suggested above.

In a given solvent, the excited state singlet lifetimes of **1**–**3** and fluorescence quantum yields of **1**–**4** do not change within the corresponding experimental uncertainties (see Experimental); the highest fluorescence yields are measured in toluene.

The very short singlet lifetime of fullerenes makes it unsuitable to probe any dendritic protection effects since the very fast intrinsic singlet excited state deactivation of fullerenes (around 1 ns) is expected to be much faster than the time needed for bimolecular quenching processes. Thus, in order to test protective effects, the study of the much longer triplet lifetimes (hundreds of ns in air-equilibrated solutions) can be more advantageous, also when considering the high intersystem crossing yield of fulleropyrrolidines ($\geqslant$90%).[20]

The shape and position of triplet-triplet transient absorption spectra are practically the same for **1**–**4** in all the investigated solvents. As an example the spectrum of **4** in CH_2Cl_2 is reported in Fig. 6, which is quite comparable to those of simpler fulleropyrrolidines previously reported.[21] By contrast, the triplet lifetimes steadily increase on passing from **1** to **4**, as displayed in the inset of Fig. 6 and summarized in Table 2.

The differences between triplet lifetimes measured in air-equilibrated solutions (AER) with respect to the corresponding values in air-free samples (DEA) is attributable to oxygen quenching, a well investigated phenomenon in fullerene photochemistry.[20] This originates from a triplet-singlet energy transfer process following light irradiation of fullerenes (F) in the presence of dioxygen; the whole reaction can be schematized as follows:

$$F \xrightarrow{h\nu} {}^1F^* \xrightarrow{ISC} {}^3F^* \xrightarrow{O_2} F + {}^1O_2^* \qquad (1)$$

where ISC denotes singlet (^{1}F*) to triplet (^{3}F*) intersystem crossing, and $^1O_2$* stands for $O_2(^1\Delta_g)$, commonly called "singlet oxygen". The occurrence of the bimolecular energy transfer process described in eqn. (1) has been probed by monitoring the diagnostic $^1O_2$* luminescence band centred at 1270 nm,[22] whose relative intensity in a given solvent can be taken to evaluate the relative yields of singlet oxygen generation (Fig. 3–5).[23] It must be pointed out that the concentration of **1**–**4** under typical experimental conditions for spectroscopic investigations (10^{-6}–10^{-5} M) is orders of magnitude lower than that of molecular oxygen in air-equilibrated organic solvents (10^{-2}–10^{-3} M).[24]

For **1**–**4** interesting trends can be obtained from the analysis of triplet lifetimes in air-equilibrated solutions (Table 2) and of the relative yields of formation of singlet oxygen, as derived from the $^1O_2$* NIR luminescence band intensities (Fig. 3–5). A steady increase of lifetimes is found by increasing the dendrimer size in all solvents, suggesting that dendritic wedges are able to partially shield the fullerene core from contacts with dioxygen molecules.[5b–d] This hypothesis can be supported by the fact that the increase is particularly marked in polar

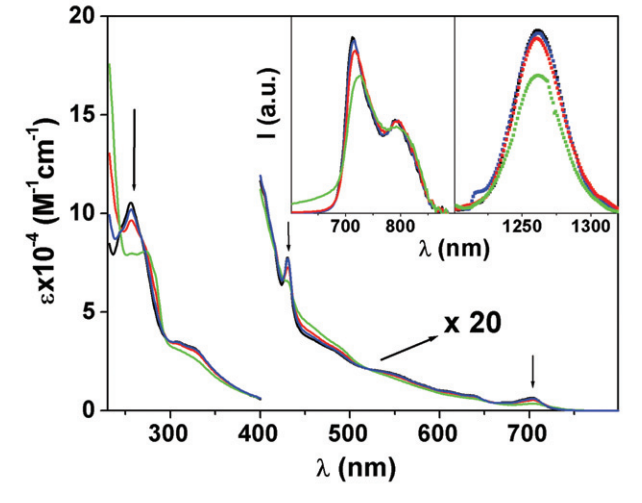


Fig. 4 Absorption spectra of **1**–**4** in CH_2Cl_2 solution at 298 K; above 400 nm a scaling factor of 20 is applied. Inset: fluorescence (left, λ_{exc} = 370 nm, O. D. = 0.30) and sensitised singlet oxygen luminescence spectra (right, λ_{exc} = 480 nm, O. D. = 0.20) of **1**–**4**. **1** (black), **2** (blue), **3** (red), **4** (green). The ε values of **2**–**4** are estimated according to the procedure described in the text.

Table 1 Fluorescence data and singlet excited state lifetimes at 298 K.[a]

	$PhCH_3$			CH_2Cl_2			CH_3CN		
	λ_{max}/nm[b]	$\Phi \times 10^4$	τ/ns	λ_{max}/nm[b]	$\Phi \times 10^4$	τ/ns	λ_{max}/nm[b]	$\Phi \times 10^4$	τ/ns
1	715	8	1.3	712	6	1.3	–[c]	–[c]	–[c]
2	715	8	1.3	715	6	1.2	716	5	1.3
3	718	8	1.4	716	6	1.2	722	6	1.3
4	725	7	1.5	726	5	1.6	728	6	1.5

[a] Fluorescence spectra and quantum yields (Φ) were obtained upon excitation at 370 nm; excited state lifetimes are upon excitation at 337 nm (see Experimental). [b] From spectra corrected for the photomultiplier response. [c] Not soluble in this solvent.

CH_3CN, where a better shielding of the fullerene chromophore is expected (see above); in this case a 45% lifetime prolongation is found in passing from **2** to **4** (23% and 28% only for $PhCH_3$ and CH_2Cl_2, respectively). It must be emphasized that triplet lifetimes of **4** in the three solvents are rather different from each other, likely reflecting specific solvent-fullerene interactions that affect excited state deactivation rates. This suggests that, albeit a dendritic effect is evidenced, even the largest wedges are not able to provide complete shielding of the central fulleropyrrolidine core; indeed, this can be expected in light of the dendrimer structures. In any case the dendritic wedges are able to reduce the singlet oxygen sensitization capability of the fullerene chromophore, and **4** exhibits the lowest singlet oxygen sensitization yield in all the investigated solvents (Fig. 3–5).

Notably, in any solvent, the triplet lifetimes in *oxygen-free* solutions are also constantly increased by enlarging the dendrimers' size (Table 2). This demonstrates that molecular oxygen is not the only potential quencher of fullerene triplet states in solution. This result is not surprising since long-lived triplet states are known to be quenched by solvent impurities such as stabilizers and/or paramagnetic ions,[25] which are commonly present in non-negligible amounts in spectroscopic grade solvents. This trend in triplet lifetimes of air-purged samples may be taken as a further proof of a protective dendritic effect in this series of dendrimers **1**–**4**. Our results compare interestingly with those of Schwell *et al.*,[26] who reported photophysical investigations on a methanofullerene chromophore bearing two large dendrimeric poly(aryl)acetylene units. In that case no appreciable changes in the absorption, luminescence, and singlet oxygen sensitization yields were observed in passing from the reference methanofullerene molecule to the fullerodendrimer.[26] This is attributable to the high rigidity of the dendritic wedge, which prevents close through-space distances between the core and the periphery, unlike our present case.

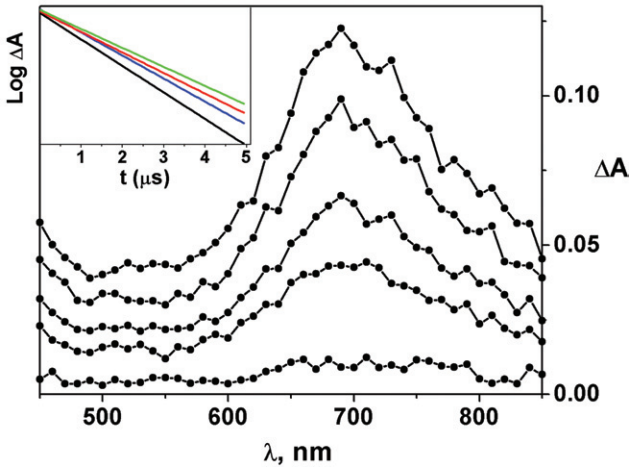


Fig. 6 Transient absorption spectrum of **4** at 298 K in CH_2Cl_2 air-equilibrated solution upon laser excitation at 355 nm (energy = 3 mJ per pulse). The spectra were recorded at delays of 100, 300, 600, 900, and 2000 ns following excitation. The inset shows the different decay time profiles of ΔA (700 nm) for the whole series of compounds: **1** (black), **2** (blue), **3** (red), **4** (green).

Incorporation in sol-gel glasses and optical limiting properties

Several studies on fullerene derivatives have shown the great potential of this class of materials for optical limiting applications.[27] In effect, the transmission of fullerene solutions decreases upon increasing the light intensity. For short pulses (ps), the limiting action is ascribed to pure reverse saturable absorption (RSA) whereas for longer pulses (ns–μs) additional mechanisms of mainly thermal origin are invoked.[28] Even if these solutions are efficient optical limiters, the use of solid devices is largely preferred for practical applications due to their greater ease of handling. Therefore, crystalline films of C_{60} have been studied, but found to be inefficient against pulses longer than tens of ps. This result is ascribed to a fast de-excitation of the laser-created excited state due to the interactions of neighbouring C_{60} molecules in the solid phase. In contrast, it has been shown that C_{60} keeps its limiting properties after inclusion in solid matrices such as sol-gel glasses,[29] polymethyl methacrylate (PMMA) matrices[30] and glass-polymer composite samples.[31] As far as sol-gel glasses are concerned, faster de-excitation dynamics and reduced triplet yields are typically observed when compared to the solutions. The latter observations are mainly explained by two factors: (*i*) perturbation of the molecular energy levels due to the interactions with the sol-gel matrix and (*ii*) interactions between neighbouring fullerene spheres due to aggregation.[28] Therefore, the encapsulation of the C_{60} core evidenced by the photophysical studies of fullerodendrimers **1**–**4** might be useful to prevent such undesirable effects.

Incorporation of fullerodendrimers **1**–**4** in the sol-gel glasses was easily achieved by soaking mesoporous silica glasses[28] with a solution of **1**–**4**. In all the cases, the resulting glass composites were dark brownish. Since the pore diameter is small, the molecules should be relatively well dispersed in the samples. This assumption is also supported by the linear optical absorption spectra. The spectra contain pronounced vibronic

Table 2 Triplet lifetimes as determined by transient absorption at 298 K in air-equilibrated (AER) and oxygen-free (DEA) solutions

	$PhCH_3$		CH_2Cl_2		CH_3CN	
	AER/ns	DEA/μs	AER/ns	DEA/μs	AER/ns	DEA/μs
1	279	34.0	598	26.3	–[a]	–[a]
2	304	37.9	643	27.4	330	14.0
3	318	39.4	732	30.1	412	21.7
4	374	42.5	827	34.6	605	25.5

[a] Not soluble in this solvent.

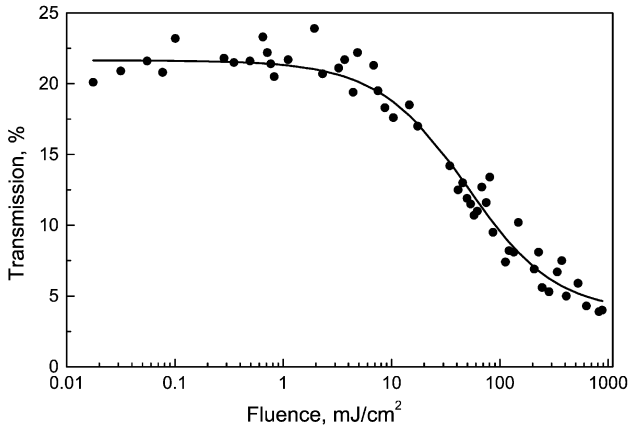


Fig. 7 Transmission *vs.* incident fluence at 532 nm of a sol-gel sample containing compound **3**.

structures that suggest only weak intermolecular fullerene-fullerene interactions; such vibronic features are absent in solutions containing aggregates as well as in crystalline films of fullerenes. Indeed, the spectra of the sol-gel samples obtained from **1**–**4** are similar to those obtained in solutions where no aggregates are present. It is therefore reasonable to conclude that the samples contain mainly well-dispersed fullerodendrimer molecules.

In order to evaluate the potential of the doped samples for optical limiting, their transmission has been determined as a function of excitation intensity. The excitation source is the frequency-doubled Nd:YAG laser emission at a wavelength of 532 nm. The pulse duration is about 30 ps, which is considerably shorter than the intersystem crossing time and the observed increase in absorption is dominated by the population of the excited singlet state. The optical transmission as a function of the fluence of the laser pulses is shown in Fig. 7 for a sol-gel sample containing compound **3**. Similar results have been obtained with the other compounds. For all the compounds, the transmission remains nearly constant for fluences lower than 3 to 10 mJ cm^{-2}. When the intensity increases above this threshold, the effect of induced absorption appears, and the transmission diminishes rapidly, thus showing the potential of these materials for optical limiting applications.

Conclusions

Poly(aryl ether) dendritic branches terminated with peripheral triethyleneglycol chains have been attached to C_{60} by the 1,3-dipolar cycloaddition of the azomethine ylides generated *in situ* from the corresponding aldehydes and *N*-methylglycine. The resulting fullerodendrimers have been characterized by electrospray mass spectrometry (ESMS), which appears to be a particularly interesting analytical tool for the unambiguous structural assignment of such high molecular weight fullerene derivatives. The results of the photophysical investigations reveal that, by enlarging the dendrimer size, changes of the core solvation environment occur, most likely as a consequence of a tighter contact between the fullerene unit and the external dendritic wedges due to favourable electronic donor/acceptor interactions.[19] This provides some shielding of the fulleropyrrolidine chromophore from contacts with external molecules such as dioxygen. As a consequence, a reduction of the potent singlet oxygen sensitizing character of the fullerene unit is obtained. Finally, thanks to their high solubility, the fullerodendrimers have been easily incorporated in mesoporous silica glasses and preliminary measurements on the resulting doped samples have revealed efficient optical limiting properties. Further studies are now underway in order to determine the influence of the dendritic branches on the optical limiting behaviour of these composite materials.

Experimental

General methods

Reagents and solvents were purchased as reagent grade and used without further purification. Compounds **5**–**8** were prepared according to a previously reported procedure.[11] 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. For 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, with 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.

Syntheses

General procedure for the synthesis of dendritic benzaldehydes 9–12. A mixture of the appropriate dendritic benzylic alcohol (1 equiv.) and MnO_2 (10 equiv.) in CH_2Cl_2 was stirred vigorously for 3 to 6 h. The mixture was filtered and evaporated to dryness under reduced pressure. The crude product was then purified as outlined in the following text.

9.. It was prepared from **5** and purified by column chromatography (SiO_2, Et_2O–acetone 7 : 3) to give **9** as a colourless glassy product: yield 84%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.38 (s, 6H), 3.53–3.73 (m, 16H), 3.87 (t, $J = 5$ Hz, 4H), 4.16 (t, $J = 5$ Hz, 4H), 6.77 (t, $J = 2$ Hz, 1H), 7.25 (d, $J = 2$ Hz, 2H), 9.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 58.76, 67.57, 69.27, 70.31, 70.39, 70.58, 71.65, 107.69, 107.99, 138.03, 160.13, 191.58.

10.. It was prepared from **6** and purified by column chromatography (SiO_2, Et_2O–acetone 7 : 3) to give **10** as a colourless glassy product: yield 80%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.38 (s, 12H), 3.53–3.76 (m, 32H), 3.85 (t, $J = 5$ Hz, 8H), 4.12 (t, $J = 5$ Hz, 8H), 5.01 (s, 4H), 6.46 (t, $J = 2$ Hz, 2H), 6.58 (d, $J = 2$ Hz, 4H), 6.84 (t, $J = 2$ Hz, 1H), 7.08 (d, $J = 2$ Hz, 2H), 9.89 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 59.01, 67.47, 69.61, 70.54, 70.61, 70.78, 71.88, 101.16, 106.03, 106.17, 108.23, 108.61, 138.42, 159.97, 160.24, 191.79.

11.. It was prepared from **7** and purified by column chromatography (SiO_2, Et_2O–acetone 2 : 3) to give **11** as a colourless glassy product: yield 82%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.35 (s, 24H), 3.51–3.70 (m, 64H), 3.82 (t, $J = 5$ Hz, 16H), 4.07 (t, $J = 5$ Hz, 16H), 4.95 (s, 8H), 5.01 (s, 4H), 6.43 (t, $J = 2$ Hz, 4H), 6.54 (t, $J = 2$ Hz, 2H), 6.57 (d, $J = 2$ Hz, 8 H), 6.64 (d, $J = 2$ Hz, 4H), 6.85 (t, $J = 2$ Hz, 1H), 7.08 (d, $J = 2$ Hz, 2H), 9.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 58.90, 67.32, 69.51, 69.86, 70.10, 70.42, 70.50, 70.66, 71.78, 100.95, 101.53, 105.91, 106.23, 108.15, 108.42, 138.25, 138.45, 138.82, 159.95, 160.14, 191.71.

12.. It was prepared from **8** and purified by column chromatography (SiO_2, CH_2Cl_2–acetone 2 : 3) to give **12** as a colourless glassy product: yield 95%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 3.35 (s, 48H), 3.50–4.15 (m, 192H), 4.95 (m, 28H), 6.30–6.80

(m, 42H), 6.85 (t, $J = 2$ Hz, 1H), 7.09 (d, $J = 2$ Hz, 2H), 9.87 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 58.95, 67.39, 69.57, 69.91, 70.49, 70.55, 70.71, 71.84, 101.03, 101.48, 106.02, 106.39, 108.23, 138.92, 160.01, 191.74.

General procedure for the synthesis of fullerodendrimers 1–4. A mixture of the appropriate dendritic benzaldehyde (1 equiv.), C_{60} (1 equiv.) and *N*-methylglycine (10 equiv.) in toluene was refluxed for 12 h. The mixture was cooled to room temperature, filtered and evaporated to dryness under reduced pressure. The crude product was then purified as outlined in the following text.

1.. It was prepared from **9** and purified by column chromatography (SiO_2, toluene–acetone 4 : 1) followed by gel permeation chromatography (Biorads, Biobeads SX-1, CH_2Cl_2) to give **1** as a brown glassy product: yield 40%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.80 (s, 3H), 3.37 (s, 6H), 3.52–3.85 (m, 20H), 4.12 (t, $J = 5$ Hz, 4H), 4.24 (d, $J = 9.5$ Hz, 1H), 4.82 (s, 1H), 4.96 (d, $J = 9.5$ Hz, 1H), 6.46 (t, $J = 2$ Hz, 1H), 6.98 (br, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 40.05, 59.06, 67.50, 69.02, 69.57, 69.89, 70.55, 70.61, 70.79, 71.91, 83.60, 101.99, 135.69, 136.46, 136.57, 139.22, 139.59, 139.84, 140.10, 141.66, 141.79, 141.92, 142.01, 142.11, 142.55, 142.95, 143.13, 144.36, 144.60, 144.68, 145.24, 145.41, 145.75, 145.92, 146.08, 146.29, 146.42, 146.96, 147.28, 153.41, 153.58, 154.08, 156.12, 159.96; Anal. calcd. for $C_{83}H_{39}O_8N.H_2O$: C 83.34, H 3.45, N 1.17, O 12.04, found: C 83.61, H 3.49, N 1.17, O 11.73.

2.. It was prepared from **10** and purified by column chromatography (SiO_2, toluene–acetone 4 : 1) followed by gel permeation chromatography (Biorads, Biobeads SX-1, CH_2Cl_2) to give **2** as a brown glassy product: yield 37%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.82 (s, 3H), 3.38 (s, 12H), 3.52–3.74 (m, 32H), 3.83 (t, $J = 5$ Hz, 8H), 4.08 (t, $J = 5$ Hz, 8H), 4.23 (d, $J = 9.5$ Hz, 1H), 4.82 (s, 1H), 4.93 (d, $J = 9.5$ Hz, 1H), 4.98 (s, 4H), 6.41 (t, $J = 2$ Hz, 2H), 6.50–6.65 (m, 5H), 7.08 (br, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 39.93, 40.04, 53.41, 59.05, 67.41, 68.99, 69.43, 70.01, 70.55, 70.63, 70.77, 71.91, 83.43, 100.79, 101.16, 102.52, 105.84, 106.68, 135.70, 136.24, 136.57, 139.14, 139.41, 139.78, 140.02, 140.12, 141.57, 141.62, 141.68, 141.89, 141.92, 141.97, 142.00, 142.09, 142.19, 142.53, 142.64, 142.92, 142.97, 144.31, 144.55, 144.65, 145.01, 145.11, 145.22, 145.45, 145.49, 145.75, 145.91, 146.04, 146.12, 146.18, 146.28, 146.42, 146.80, 147.27, 153.36, 154.03, 156.07, 160.05; Anal. calcd. for $C_{111}H_{79}O_{18}N$: C 77.75, H 4.64, N 0.82, O 16.79, found: C 77.74, H 4.67, N 0.85, O 16.74.

3.. It was prepared from **11** and purified by column chromatography (SiO_2, toluene–acetone 3 : 2) followed by gel permeation chromatography (Biorads, Biobeads SX-1, CH_2Cl_2) to give **3** as a brown glassy product: yield 39%; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 2.82 (s, 3H), 3.38 (s, 24H), 3.52–3.75 (m, 64H), 3.83 (t, $J = 5$ Hz, 16H), 4.09 (t, $J = 5$ Hz, 16H), 4.22 (d, $J = 9.5$ Hz, 1H), 4.82 (s, 1H), 4.90 (s, 8H), 4.94 (d, $J = 9.5$Hz, 1H), 5.03 (s, 4H), 6.43–7.09 (m, 19H), 7.08 (br, 2H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 40.02, 59.03, 67.47, 67.68, 68.97, 69.64, 69.80, 69.98, 70.55, 70.63, 70.79, 70.97, 71.90, 83.37, 101.16, 101.51, 102.66, 106.03, 106.19, 135.65, 135.68, 136.17, 136.57, 138.87, 139.33, 139.46, 139.75, 139.99, 140.08, 141.53, 141.62, 141.89, 141.97, 142.03, 142.09, 142.16, 142.44, 142.51, 142.62, 142.88, 142.92, 144.30, 144.52, 144.60, 144.92, 145.08, 145.21, 145.46, 145.72, 145.89, 146.02, 146.07, 146.16, 146.25, 146.40, 146.75, 147.23, 153.33, 153.36, 154.02, 156.09, 159.84; Anal. calcd. for $C_{167}H_{159}O_{38}N.H_2O$: C 71.48, H 5.78, N 0.50, O 22.24, found: C 71.55, H 5.88, N 0.50, O 22.07.

4.. This was prepared from **12** and purified by column chromatography (SiO_2, toluene–acetone 3 : 2) followed by gel permeation chromatography (Biorads, Biobeads SX-1, CH_2Cl_2) to give **4** as a brown glassy product: yield 44%; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.80 (s, 3H), 3.37 (s, 48H), 3.47–3.77 (m, 128H), 3.76 (t, $J = 5$ Hz, 32H), 4.10 (t, $J = 5$ Hz, 32H), 4.23 (d, $J = 9.5$ Hz, 1H); 4.92 (m, 30H), 6.44–7.05 (m, 43H), 7.12 (br, 2H); Anal. calcd. for $C_{279}H_{319}O_{78}N.CH_2Cl_2$: C 67.05, H 6.37, N 0.28, O 24.88, found: C 66.73, H 6.53, N 0.28, O 24.86.

Electrospray mass spectrometry (ESMS)

Positive ES mass spectra were obtained on a ES triple quadrupole mass spectrometer Quattro II with a mass-to-charge (m/z) ratio range extended to 8000 (Micromass, Altrincham, UK). The electrospray source was heated to 45 °C. The sampling cone voltage (V_c) was at 160 V to allow the transmission of ions with $m/z > 4000$ without fragmentation processes. Under these conditions reproducible spectra were also obtained. Sample solutions were introduced into the mass spectrometer source with a syringe pump (Harvard type 55 1111: Harvard Apparatus Inc., South Natick, MA, USA) with a flow rate of 6 μL min^{-1}. Calibration was performed using protonated horse myoglobin. Scanning was performed in the MCA (multi channel analyzer) mode, and several scans were summed to obtain the final spectrum.

Samples for ESMS were prepared by dissolving the compound under study in a solution of CH_2Cl_2 containing 1% formic acid to achieve a concentration of 10^{-4} M. After stirring at room temperature for 1 min, the clear red solution was directly analyzed by ESMS.

Spectroscopic and photophysical measurements

The photophysical investigations were carried out in toluene, dichloromethane, and acetonitrile (Carlo Erba, spectrofluorimetric grade). The samples were normally placed in fluorimetric 1 cm path cuvettes. Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter (continuous 150 W Xe lamp), equipped with a Hamamatsu R-928 photomultiplier tube. The corrected spectra were obtained *via* a calibration curve determined with a procedure described earlier.[32] Fluorescence quantum yields obtained from spectra on an energy scale (cm^{-1}) were measured with the method described by Demas and Crosby[33] using as standards air-equilibrated solutions of $[Os(phen)_3]^{2+}$ in acetonitrile ($\Phi_{em} = 0.005$).[34]

The steady-state IR luminescence spectra were obtained with an apparatus available at the Chemistry Department of the University of Bologna (Italy) and described in detail earlier.[32] A continuous 450 W xenon lamp was used as the light source; excitation was performed at 480 nm. The determination of the relative yields of singlet oxygen sensitization in a given solvent can be obtained by monitoring the singlet oxygen luminescence intensity at 1270 nm of solutions displaying the same optical density (0.3) at the excitation wavelength.[23]

Emission lifetimes on the nanosecond time scale were determined with an IBH single photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the range of 2–40 KHz ($\lambda_{exc} = 337$ nm, 0.5 ns time resolution); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237–01 photomultiplier tube.

Transient absorption spectra in the nanosecond–microsecond time domain were obtained by means of a flash-photolysis system described in detail earlier.[35] Excitation was performed with the third harmonic (355 nm) of a Nd:YAG laser (J.K. Lasers Ltd.) with 20 ns pulse duration and 1–2 mJ of energy per pulse. Triplet lifetimes were obtained by

averaging at least five different decays recorded around the maximum of the absorption peak (680–720 nm). When necessary, oxygen was removed by at least four freeze-thaw-pump cycles by means of a diffusive vacuum pump at 10^{-6} Torr (CH_2Cl_2, PhMe) or by bubbling argon for several minutes through the solution (CH_3CN).

Experimental uncertainties are estimated to be ±7% for lifetime determinations, ±20% for emission quantum yields, and ±2 nm for absorption and emission peaks.

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).[36] The reaction was followed by FTIR, which showed that full hydrolysis of TMOS occurred within a few seconds. The condensation reaction then took place and gelation occured within 2 to 3 h, depending on the temperature, 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. During this step extensive 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. The samples were mesoporous as shown by physisorption measurements. The mean pore diameter was 3.46 nm and the maximum pore diameter was 4.9 nm with a porous volume of 0.2133 $cm^3\ g^{-1}$. The resulting silica glasses were prepared by the sol-gel process and soaked in a concentrated THF solution of compound **1**, **2**, **3** or **4**. After 30 min, the samples were removed from the solutions and dried at 40 °C for 1 h.

Optical limiting measurements

To study the optical limiting properties, the transmission of the doped glass samples was determined as a function of the incoming fluence at room temperature. 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 was used for these measurements. At this wavelength, the linear transmission of the samples was typically 40 to 60%. 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 were 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, was sent onto the same optical multichannel analyzer. The incident intensity at the sample position was changed by means of calibrated neutral density filters.

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