Photophysical, photochemical, and electrochemical properties of dendrimers with a dimethoxybenzil core†

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Three dendrimers consisting of a dimethoxybenzil core and branches that contain two (**G0**), four (**G1**), and eight (**G2**) naphthalene units at the periphery and zero (**G0**), two (**G1**), and six (**G2**) dimethoxybenzene units in the branches have been synthesized and their photophysical, photochemical, and electrochemical properties have been investigated. For comparison purposes, the properties of dimethoxybenzil (**MB**) and of a dendron containing four naphthalene and three dimethoxybenzene units (**D2**) have also been studied. The properties of the dendrimers in the ground state (absorption spectra and electrochemical behavior) are those expected for their noninteracting component units. The excited state properties, however, are substantially controlled by electronic interactions between the dimethoxybenzil core and the naphthalene units contained in the branches. In dichloromethane–chloroform 1 : 1 (v/v) solution at 298 K, energy transfer from the lowest excited state (S_1) of the naphthalene units to the lower lying S_1 excited state of the dimethoxybenzil core takes place with high efficiency. In a rigid matrix at 77 K, selective excitation of the dimethoxybenzil chromophore yields an emission band that exhibits a spectral evolution: in the millisecond time scale it shows a spectral profile very similar to the dimethoxybenzil phosphorescence, whereas in the second time scale it is very similar to the naphthalene-type phosphorescence. Energy transfer from the T_1 excited state of the dimethoxybenzil core to the T_1 excited state of the naphthalene units takes place at 77 K, but not at 298 K, because the T_1 excited state of the dimethoxybenzil core moves to energy lower than that of the naphthalene chromophore. The photochemical results show that the dimethoxybenzil core maintains its intrinsic photoreactivity toward dioxygen, and that on increasing dendrimer generation a photoreaction between core and branches predominates.

Introduction

Dendrimers[1,2] are repeatedly branched tree-like compounds, that can be synthesized with well defined composition, a high degree of order, and the possibility to contain selected chemical units in predetermined sites of their structure. These macromolecules are currently attracting the interest of a great number of scientists because of their unusual chemical, physical and biological properties and the wide range of potential applications.[3]

In the last few years, several families of dendrimers containing different chromophoric and luminophoric units have been synthesized.[4] In the dendritic structure, the electronic interaction between nearby units is usually small in the ground state, so that each unit can be independently excited and the dendrimer absorption spectrum is close to the summation of the spectra of the component units. When a single chromophoric group is in an excited state, however, the interaction with the nearby units is often strong enough to change its luminescence behavior because of formation of excimers or exciplexes[5] and the occurrence of energy[6] or electron[7] transfer processes. In suitably designed dendrimers energy transfer processes can be spatially and energetically controlled, thereby opening the way towards the construction of antenna systems for solar energy conversion,[8] luminescence sensors with signal amplification,[9] and systems capable of changing the wavelength of light.[8c,10]

Continuing our studies on dendrimers,[4a] we have investigated the photophysical, photochemical, and electrochemical properties of three dendrimers consisting of a dimethoxybenzil core and branches that contain two (**G0**), four (**G1**), and eight (**G2**) naphthalene units at the periphery and zero (**G0**), two (**G1**), and six (**G2**) dimethoxybenzene units in the branches (Scheme 1). Benzil, naphthalene, and dimethoxybenzene are well known luminescent species. In particular, both fluorescence and phosphorescence are exhibited by benzil[11] and naphthalene[11] in suitable experimental conditions, opening the possibility to investigate singlet–singlet and triplet–triplet energy transfer. For comparison purposes, the properties of

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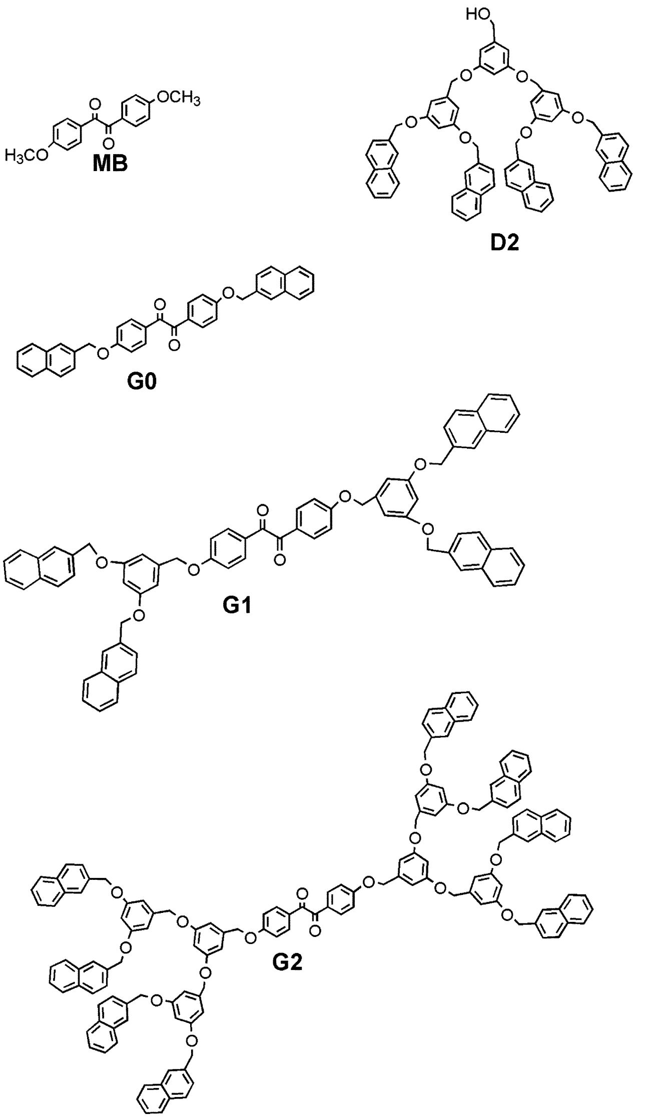


Scheme 1

dimethoxybenzil (**MB**), 2-methylnaphthalene, and of a dendron containing four naphthalene units and three dimethoxybenzene units (**D2**) have also been studied.

Results and discussion

Photophysical properties

Absorption spectra. Dendron **D2** absorbs at higher energy (λ_{max} = 275 nm) compared to **MB** (λ_{max} = 300 nm) (Fig. 1(a)). In particular, the absorption spectrum of **D2** is dominated by the four naphthalene groups, since the three dimethoxybenzene moieties, that absorb in the same spectral region, have a molar absorption coefficient ($\varepsilon_{275\ nm}$ = 2200 $M^{-1}\ cm^{-1}$)[12] smaller than that of naphthalene ($\varepsilon_{275\ nm}$ = 4300 $M^{-1}\ cm^{-1}$).[13] The absorption spectra of the dendrimers (Fig. 1(b)) show the features of both the dimethoxybenzil core, with a shoulder at 300 nm, and the dimethoxybenzene and naphthalene units contained in the branches, with a maximum at 275 nm. The number of naphthalene and dimethoxybenzene chromophores increases on increasing dendrimer generation and, as a consequence, the absorbance at 275 nm increases while the shoulder at 300 nm is practically constant. Quantitative comparison with the spectra of the model compounds shows that there is no significant interaction in the ground state. In particular, the spectrum of **G2** is almost coincident with that obtained considering the sum of the spectra of two dendrons **D2** and a **MB** unit.

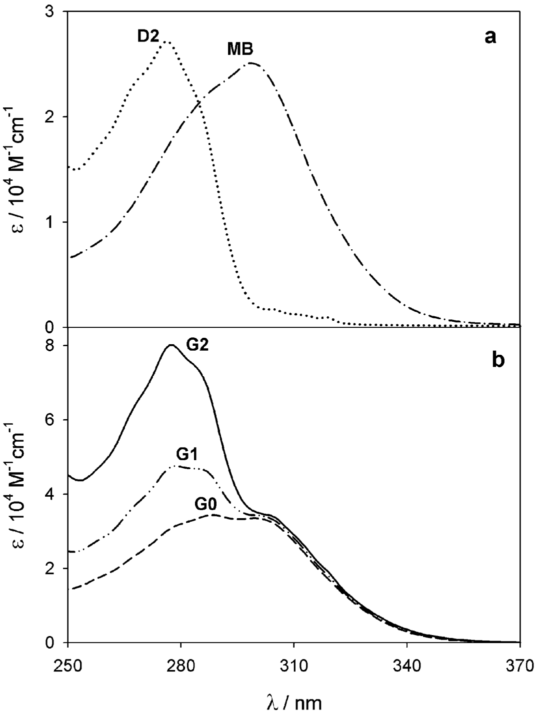


Fig. 1 Absorption spectra of **MB** and **D2** (a) and dendrimers **G0–G2** (b) in CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) at 298 K.

Fluorescence spectra and lifetimes. Upon excitation at 277 nm, dendrimers **G0–G2** show two emission bands: the first one, with maximum at 335 nm (Fig. 2), is due to the fluorescence of the naphthalene group; the second one, with

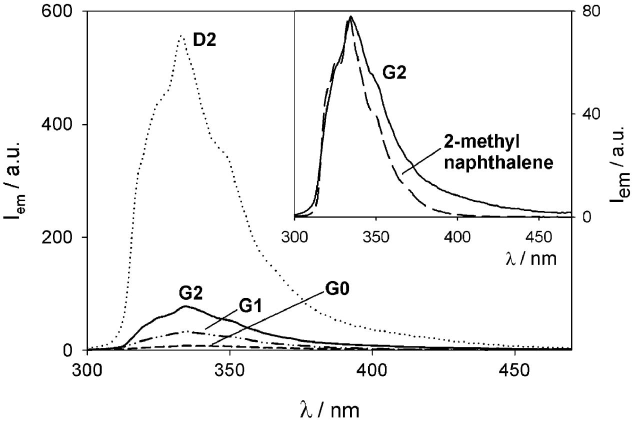


Fig. 2 Fluorescence spectra of dendrimers **G0–G2** and dendron **D2** in CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) at 298 K with the same absorbance at the excitation wavelength. λ_{ex} = 277 nm. Inset shows the normalized emission spectra of **G2** and a model compound, 2-methylnaphthalene.

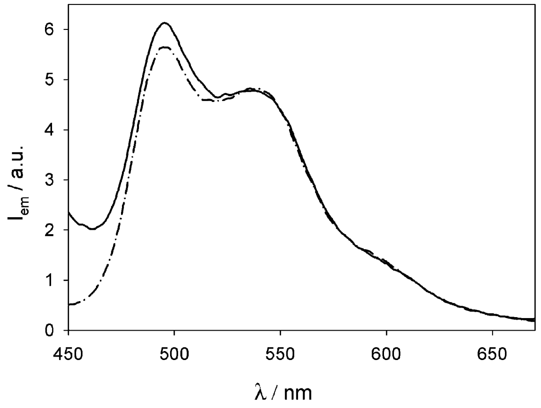


Fig. 3 Fluorescence spectra of **G2** (solid line) and **MB** (dashed-dotted line) in CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) at 298 K with the same absorbance at the excitation wavelength. λ_{ex} = 277 nm.

maximum at 495 nm and much weaker in intensity (see, for example, Fig. 3), is assigned to the dimethoxybenzil fluorescence, because of the close similarity to that recorded for **MB**. The small quantum yield of the dimethoxybenzil fluorescence is due to the close proximity of the $S_1(n\pi^*)$ and $T_1(n\pi^*)$ excited states that favors intersystem crossing.[14] The emission bands centred at 335 nm of **G1**, **G2**,[15] and **D2** show a weak tail at lower energy, compared with that exhibited by 2-methylnaphthalene (inset of Fig. 2), suggesting formation of naphthalene excimers.[16]

It should be noticed that the naphthalene-type emission in the dendrimers is strongly quenched compared to **D2**, as evidenced by the spectra displayed in Fig. 2 and the quantum yield data reported in Table 1. On the other hand, emission of the benzil core at 495 nm is sensitised. Indeed, practically coincident emission intensities at 495 nm were obtained upon excitation at 277 nm of isoabsorbing solutions of **G2** and **MB** (Fig. 3), although in the case of **G2** about 80% of the light is absorbed by naphthalene units at the excitation wavelength. Therefore, an energy transfer process from the lowest excited state (S_1) of the naphthalene units to the lower lying S_1 excited state of the dimethoxybenzil core takes place with high efficiency (Φ > 0.9).[17] A further proof of a high energy transfer efficiency comes from the fact that the excitation spectra of **G0–G2** (recorded with λ_{em} = 500 nm) are practically coincident with the corresponding absorption spectra. The quantum yield of the naphthalene type emission slightly increases on increasing dendrimer generation, most likely because of the increasing distance between the donor and acceptor partners of the energy transfer process. The photoinduced energy transfer process from the S_1 state of naphthalene to the S_1 state of the dimethoxybenzil core is active also at 77 K (Scheme 2), since a significant quenching of the naphthalene emission intensity and lifetime is observed when dendrimers **G0–G2** are compared to dendron **D2**. However, sensitization of the dimethoxybenzil has not been evidenced because its fluorescence quantum yield is so low that the corresponding band is completely covered by the much more intense phosphorescence band.

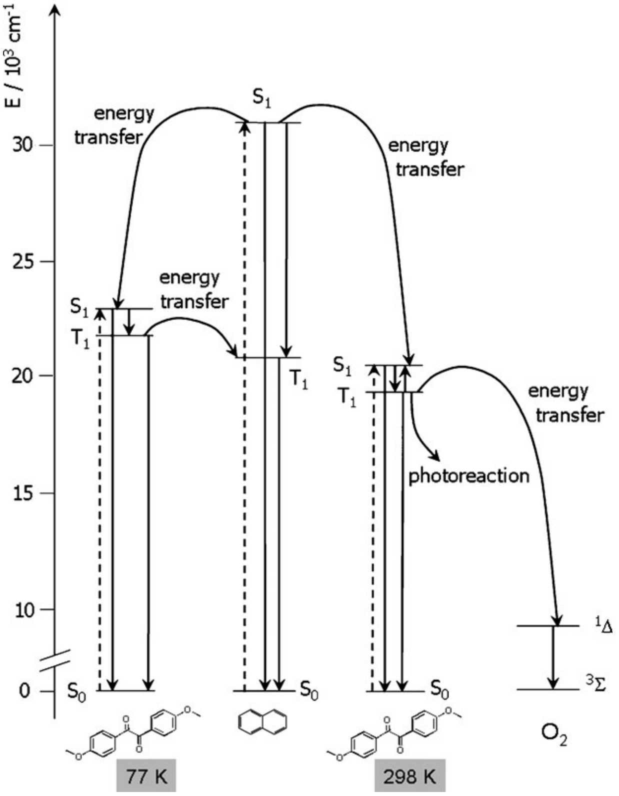
No fluorescence of the dimethoxybenzene group has been observed in dendrimers **G1** and **G2**, as expected on the basis of the behaviour of the dendron **D2** where the potentially fluorescent S_1 excited state of dimethoxybenzene is quenched by energy and electron transfer processes involving the naphthalene units.[16] Furthermore, in the case of dendrimers **G1** and **G2** another lower-lying excited state located on the core is present, so that an additional quenching channel for the fluorescent excited state of dimethoxybenzene is available.

The results obtained for **G0–G2** from fluorescence lifetime measurements are not easily interpreted because multi-exponential decays were observed due to spectral overlaps. The reference compound **MB** has a very short lifetime (<0.5 ns), while **D2** shows a biexponential decay: the shorter component is the usual naphthalene-type emission, while the longer one is assigned to an excimer emission.[16] In the case of the

Table 1 Photophysical data in dichloromethane–chloroform 1 : 1 (v/v) solution, unless otherwise noted

	Absorption		Fluorescence			Phosphorescence			
	298 K		298 K			298 K		77 K[a]	
	λ_{max}/nm	ε_{max}/M^{-1} cm^{-1}	λ_{max}/nm	Φ_{em}	τ/ns	λ_{max}/nm	τ/μs	λ_{max}/nm	τ/s
MB	300	25 000	495	3×10^{-4}	<0.5[b]	550	25	494 (492)	2.7×10^{-3} (2.7×10^{-3})
D2	276	27 200	335	2.8×10^{-2}	5.4, 66	—[c]	—[c]	480 (480)	1.2 (1.5)
G0	288	34 400	335 495	6×10^{-4} 3×10^{-4}	<0.5, 3.2[d] <0.5[b]	550	30	502 (502)	2.5×10^{-3}, 0.9 (1.4)
G1	280	47 500	335 495	1×10^{-3} 3×10^{-4}	<0.5, 3.2[d] <0.5[b]	550	30	502 (502)	1.6×10^{-3}, 1.0 (1.5)
G2	278	80 100	335 495	3×10^{-3} 3×10^{-4}	<0.5, 3.1[d] <0.5[b]	550	30	492 (518)	1.1×10^{-3}, 1.0 (1.2)

[a] Data reported in parenthesis have been obtained in dichloromethane–methanol 1 : 1 (v/v) rigid matrix at 77 K. [b] Prompt fluorescence to be distinguished from delayed fluorescence displayed in Fig. 4. [c] No emission has been observed. [d] The two lifetimes reported correspond to the naphthalene monomer emission with maximum at 335 nm and the excimer emission tail at lower energy. The value of the shorter lifetime cannot be determined with the equipment used (see Experimental section).



Scheme 2

dendrimers, the shorter component (<0.5 ns) can be assigned to the naphthalene-type emission, that is highly quenched compared to **D2**, and the longer one to the naphthalene excimer emission (see inset of Fig. 2). The small emission quantum yield of the dimethoxybenzil chromophore and the partial spectral overlap with the naphthalene excimer emission prevented a reliable estimation of the emission lifetime of the core.

Phosphorescence spectra, T_1–T_n transient absorption spectra and lifetimes. The emission spectrum recorded with a 10 μs delay for a deaerated dichloromethane–chloroform 1 : 1 (v/v) solution of **MB** shows a maximum at 548 nm (τ = 25 μs) and a shoulder at 495 nm (Fig. 4). The maximum can be attributed to the dimethoxybenzil phosphorescence. The shoulder is in the same position of the fluorescence band observed in aerated solution while it is not present in the phosphorescence spectra recorded at 77 K (*vide infra*) and is thus attributed to delayed fluorescence,[14b] *i.e.* to the thermal population at 298 K of the S_1 excited state from the T_1 one. Indeed, the ratio of emission intensities at 495 and 548 nm is not dependent on the delay time used to register the emission spectrum. This result indicates that the two emission bands originate from two states with the same lifetime, *i.e.* S_1 and T_1 are in thermal equilibrium. Similar spectra have been obtained for dendrimers **G0**–**G2** upon selective excitation of the dimethoxybenzil chromophore at 330 nm (see *e.g.* **G1** in Fig. 4). The phosphorescence intensity of isoabsorbing solutions at the excitation wavelength are slightly higher and the corresponding lifetimes are slightly longer in the case of the dendrimers compared to **MB** reference compound (Table 1). These results demonstrate that no quenching of the T_1 excited state of the dimethoxybenzil core is brought about by the naphthalene moieties and suggest that either (i) the dendritic wedges protect the dimethoxybenzil excited state by quenching from residual dioxygen or (ii) a more rigid structure of the dimethoxybenzil core in the dendrimers leads to lower non-radiative decay rate constant. On the other hand, no emission has been recorded, under the same experimental conditions, in the case of **D2**. Indeed, **D2** phosphorescence can be observed only at 77 K (*vide infra*) because the T_1 excited state of naphthalene has a very long lifetime (Table 1) that allows bimolecular quenching by impurities present even at very low concentration.

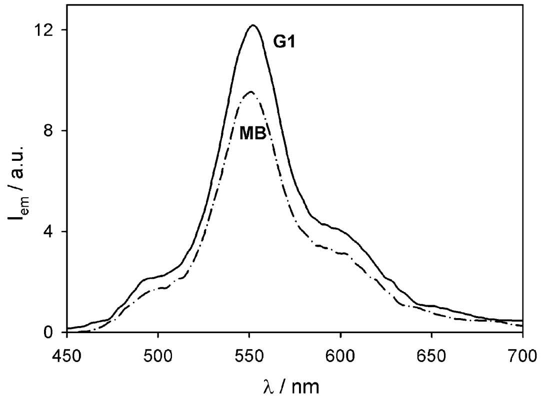


Fig. 4 Phosphorescence spectra of **MB** and **G1** in deaerated CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) solution at 298 K, under the same experimental conditions. λ_{ex} = 330 nm.

Laser-flash photolysis experiments performed on **MB** and dendrimers **G0**–**G2** in deaerated dichloromethane–chloroform 1 : 1 (v/v) solutions showed, upon excitation of the dimethoxybenzil moiety (λ_{ex} = 355 nm), transient absorption spectra characteristic of $T_1 \rightarrow T_n$ transitions of the dimethoxybenzil chromophore.[18] Time evolution of this spectral changes, *e.g.* at λ_{max} = 480 nm, was not monoexponential and depended on laser intensity and chromophore concentration. The decays can be fitted by a combination of a first- and second-order process (see experimental section), *i.e.* intrinsic deactivation of T_1 and bimolecular triplet–triplet annihilation.[19] The triplet excited state lifetimes (first-order component) are in very good agreement with data found by analysing phosphorescence intensity decays.[20] Triplet–triplet annihilation rate constants (k_{T-T}), measured under the same experimental conditions (λ_{ex} = 355 nm, λ_{abs} = 480 nm), decreased in going from **MB** ($k_{T-T} = 1.2 \times 10^6\ M^{-1}\ s^{-1}$) to dendrimers (*e.g.*, in the case of **G1** $k_{T-T} = 0.5 \times 10^6\ M^{-1}\ s^{-1}$). This experimental result shows that, as expected, the dimethoxybenzil core in the dendrimers is protected against self-quenching by the dendritic branches.

In dichloromethane–chloroform 1 : 1 (v/v) rigid matrix at 77 K, **MB** and **D2** show two phosphorescence bands very close in energy (Fig. 5(a)). The main differences are: (i) the vibrational structure present only in the phosphorescence of **D2**, (ii) the lifetime values: 2.7 ms for **MB** and 1.2 s for **D2** (Table 1) and (iii) the phosphorescence quantum yield much lower for naphthalene than that of benzil.[11] The phosphorescence of **MB** is assigned to the nπ* triplet excited state (T_1) of the dimethoxybenzil chromophore, and that of **D2** to the ππ* T_1 excited state of the naphthalene unit, as evidenced by

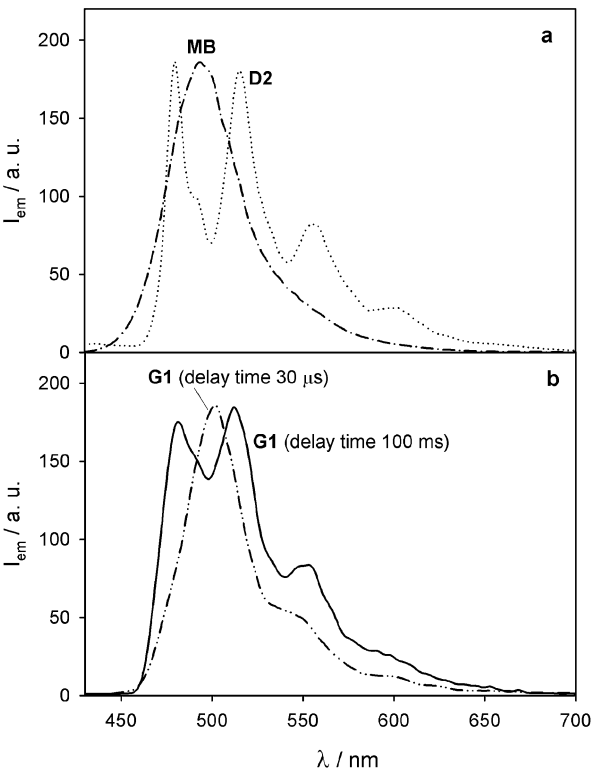


Fig. 5 Phosphorescence spectra of **MB** and **D2** (a) and of dendrimers **G1** (b) in CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) at 77 K. λ_{ex} = 330 nm.

comparison of the phosphorescence bands of 2-methylnaphthalene.[16] Under the same experimental conditions, dendrimers **G0–G2** show a complex behaviour: upon selective excitation of the dimethoxybenzil chromophore at 330 nm, the phosphorescence spectrum recorded with a relatively short delay (30 μs) shows a spectral profile very similar to that observed for **MB**, while recorded with a longer delay (100 ms) is very similar to the naphthalene-type phosphorescence (see *e.g.*, Fig. 5(b)). Correspondingly, two lifetimes have been observed (Table 1): a shorter one (ms time scale) assigned to the dimethoxybenzil chromophore, and a longer one (second time scale) due to the naphthalene moiety. The T_1 excited states of naphthalene and dimethoxybenzil units are very close in energy (Fig. 5(a)), but spectral evolution of the phosphorescence band for dendrimers **G0–G2** and observation of naphthalene phosphorescence upon selective excitation of dimethoxybenzil core are indicative of an energy transfer process from the dimethoxybenzil to the naphthalene chromophore (Scheme 2). The efficiency of this process is low, as demonstrated by the slight decrease of dimethoxybenzil triplet excited state lifetime (Table 1), and an estimation of the naphthalene sensitization efficiency and rate constant is difficult. Indeed, quantitative measurements of emission intensities at 77 K are difficult, especially in the present case since the naphthalene phosphorescence quantum yield is much lower than that of benzil.[11]

Contrary to what happens at 77 K, at 298 K there is no evidence for energy transfer from the T_1 excited state of dimethoxybenzil to that of naphthalene in dendrimers **G0–G2**. The emission quantum yield and lifetime of the T_1 excited state of the dimethoxybenzil unit at room temperature is slightly higher in the case of dendrimers compared to **MB** (Table 1) and no transient absorption features typical of naphthalene (2-methylnaphthalene shows a transient absorption spectrum with λ_{max} at *ca.* 400 nm) has been observed upon selective excitation of the dimethoxybenzil core (λ_{ex} = 355 nm). The lack of energy transfer at room temperature can be explained considering that the dimethoxybenzil phosphorescence shows a quite strong blue shift in going from 298 to 77 K, as expected for a nπ* transition where lack of solvent repolarization in rigid matrix leads to an increase of the corresponding excited state energy. A much less pronounced shift is expected for the naphthalene T_1 excited state, because of its ππ* character. As a consequence, the lowest T_1 excited state in the dendrimers is located on the dimethoxybenzil at 298 K and on the naphthalene at 77 K.

Another interesting aspect of the phosphorescence bands observed for these dendrimers is that only in the case of **G2** there is a substantial solvent effect. The **G2** phosphorescence is red-shifted compared to **MB**, **G0** and **G1** in dichloromethane–methanol rigid matrix and blue-shifted in dichlormethane–chloroform (Table 1). The peculiar behaviour of **G2** can be due to a different degree of back-folding of the dendrons in the two solvent mixtures, thus creating an environment of different polarity from the bulk of the solution.

In aerated solution, all the examined compounds are able to transfer energy to dioxygen with high efficiency as shown by the observation of the singlet dioxygen emission band at 1260 nm.

Photochemical properties

Upon irradiation at 313 nm of an air-equilibrated CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) solution of **MB**, strong changes in the absorption spectra are observed (Fig. 6(a)): the

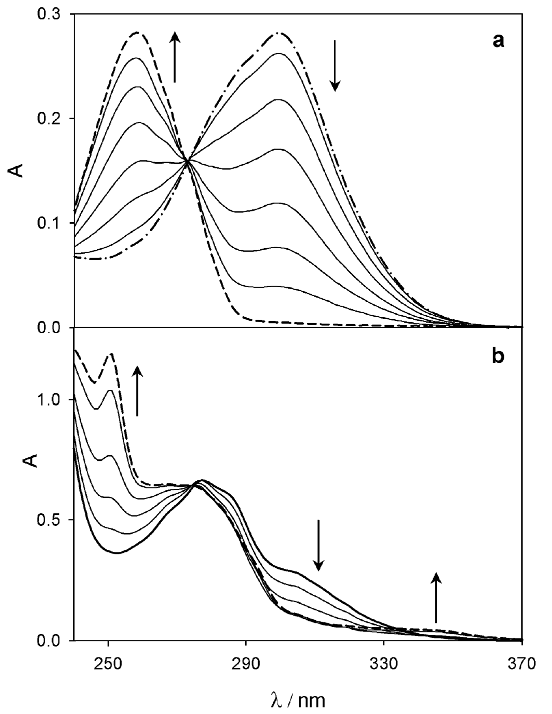


Fig. 6 Absorption changes of **MB** (a) and **G2** (b) in air-equilibrated CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) solution during irradiation at 313 nm.

characteristic dimethoxybenzil band at 300 nm disappears and a new one with maximum at 255 nm increases with an isosbestic point at 273 nm. The reaction quantum yield, measured from the disappearance of the band at 300 nm, is 0.09 in air-equilibrated solution, while it is negligible (<0.005) in deaerated solution where no absorption change was observed for irradiation times comparable to those of the air-equilibrated experiments. Clearly, dioxygen is involved in the photochemical reaction, likely due to the formation of benzoyl peroxide, as already reported.[21]

Fig. 6(b) shows the absorption changes recorded upon irradiation at 313 nm of an air-equilibrated CH_2Cl_2–$CHCl_3$ 1 : 1 (v/v) solution of **G2**. Although the photoreaction quantum yield is similar (0.07) to that obtained for **MB**, substantial qualitative differences from the **MB** photoreactivity can be observed: (i) two new absorption bands appear upon irradiation, one at higher energy (λ_{max} = 250 nm) compared to that of dimethoxybenzil, and one at lower energy (λ_{max} $\approx$350 nm); (ii) no effect of oxygen has been observed (Φ = 0.07 both in air equilibrated and deaerated solutions).

In the case of air-equilibrated solutions of **G0** and **G1** irradiation at 313 nm caused spectral changes that, at the beginning, were similar to those observed under the same experimental conditions for **MB**, *i.e.* disappearance of the band at 300 nm and increase of a new one at higher energy. On going on with irradiation, however, a new band at 250 nm and a red tail (λ_{max} $\approx$350 nm) were formed, reminiscent of the photochemical reactivity of **G2**. Two different families of spectra, characterized by different isosbestic points, were indeed obtained, indicating the occurrence of two successive photochemical reactions. In deaerated solution, the photochemical reactivity of **G0** and **G1** is quite similar to that exhibited by **G2**, but with a much lower quantum yield (see Table 2).

Irradiation at 313 nm of a deaerated solution containing **MB** (4×10^{-5} M) and **D2** (4×10^{-4} M) leads to spectral changes similar to those observed in the case of **G2**: the dimethoxybenzil band disappears and a new band at lower energy (λ_{max} $\approx$350 nm) increases.

In conclusion, the results obtained show that the dimethoxybenzil core maintains its photoreactivity toward dioxygen, and that on increasing dendrimer generation the branches perhaps protect the core towards reaction with dioxygen, but introduce a new reaction channel involving the dendron itself.

Electrochemical characterization

Table 2 Photoreaction quantum yield[a] upon irradiation at 313 nm in dichloromethane solution at 298 K

	Φ_{react}	
	Air-equilibrated solution	Deaerated solution
MB	0.09	<0.005
G0	0.11	0.007
G1	0.10	0.01
G2	0.07	0.07

[a] Reported quantum yields were obtained by extrapolation to time zero of the initial part of the photoreaction.

The cyclic voltammogram recorded for **MB** in dichloromethane/$TBAPF_6$ solution shows two reduction processes: the first one ($E_{1/2}$ = −1.22 V *vs.* SCE) is completely reversible, while the second one ($E_{1/2}$ = −1.47 V *vs.* SCE) shows some degree of chemical irreversibility. The spectroelectrochemical characterization of the monoanionic species $\mathbf{MB}^-$ has been performed in an OTTLE cell and evidences the appearance of new absorption bands at 370 and 600 nm.

In the cathodic region **G2** undergoes two one-electron reduction processes likely centred on the dimethoxybenzil core ($E_{1/2}$(I) = −1.19 V $E_{1/2}$(II) = −1.66 V *vs.* SCE), but the second peak is cathodically shifted and presents an higher degree of chemical irreversibility. The spectroelectrochemical investigation of the monoanionic species of **G2** confirms that the first reduction process involves the dimethoxybenzil core since the absorption changes are similar to those observed for the reduction of **MB**. The spectroelectrochemistry in correspondence of the second reduction process is prevented by the narrower potential window available in the spectroelectrochemical experimental conditions.

The electrochemical reversibility (high rate of heterogeneous electron transfer) of the first reduction process of the benzyl core in **G2** shows that there is no significant site isolation effect in the dendritic structure. On the other hand, the shift of the second reduction process towards more negative potentials can be attributed to a lower stabilization of the dianionic species in the environment created by the dendrons compared to the $\mathbf{MB}^{2-}$ species in the bulk of the solution.

In the anodic region the cyclic voltammogram of **G2** presents a multielectronic chemically irreversible process, that can be assigned to the oxidation of the dimethoxybenzene units of the dendrons[22] (E_{pa} = +1.93 V *vs.* SCE at 0.2 V s^{-1}).

Conclusions

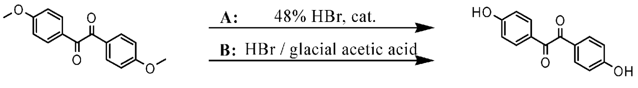
We have investigated the photophysical, photochemical, and electrochemical properties of **G0**, **G1**, and **G2** dendrimers and of their core (**MB**) and branches (**D2**) reference compounds. The properties of the dendrimers in the ground state (absorption spectra and electrochemical behavior) are those expected for their dimethoxybenzil, naphthalene, and dimethoxybenzene noninteracting units. The excited state properties, however, are substantially controlled by electronic interactions between the dimethoxybenzil core and the naphthalene units contained in the branches, whereas the dimethoxybenzene units play a less important role. In this family of dendrimers multiple photoinduced energy transfer processes take place: from the lowest singlet excited state (S_1) of the naphthalene units to that of the dimethoxybenzil core both at 298 and 77 K and from the T_1 excited state of the dimethoxybenzil core to the T_1 excited state of the naphthalene units at 77 K, but not at 298 K. The latter is a quite unusual result in dendritic species. At 298 K, the T_1 excited state the dimethoxybenzil core moves to lower energy, thus preventing the photoinduced energy transfer. As far as the photochemical behavior is concerned, the dimethoxybenzil unit maintains its intrinsic photoreactivity toward dioxygen even when it belongs to the dendrimer core, and on increasing dendrimer generation a photoreaction between core and branches also takes place.

Experimental

Synthetic procedure

4,4′-Dimethoxybenzil (**MB**) is commercially available (Fluka).

4,4′-Dihydroxybenzil



MB

Route A. 4,4′-Dimethoxybenzil **MB** (2.0 g; 7.4 mmol) and hexadecyltributylphosphonium bromide (760 mg; 1.5 mmol) as catalyst in aqueous HBr (48%; 40 ml), were heated to reflux for 6 h. The reaction mixture was then poured into water and the mixture extracted several times with ethyl acetate. The organic phase was dried with $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2; dichloromethane–acetone 5 : 1) yielding 100 mg of a yellowish solid.

Route B. 4,4′-Dimethoxybenzil **MB** (2.0 g; 7.4 mmol) was heated to reflux for 3 h in a mixture of aqueous HBr (48%) and glacial acetic acid (50 ml; 1 : 1 v/v). The reaction mixture was poured into water and then extracted several times with ethyl acetate. The organic phase was washed two times with water, dried with $MgSO_4$ and the solvent removed under reduced pressure. The residue was purified by column chromatography (SiO_2; dichloromethane–acetone 5 : 1) yielding a yellowish solid.

TLC (SiO_2): R_f = 0.5 (dichloromethane–acetone 5 : 1 v/v).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 6.78 (AA‘BB’, 4H, $^3J_{HH}$ = 8.9 Hz), 7.73 (AA‘BB‘, 4H, $^3J_{HH}$ = 8.9 Hz).

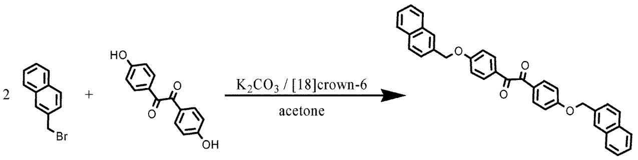
^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ [ppm] 115.82, 125.04, 132.58, 163.65, 194.31 (C_{ar}), 194.31 (ketone-*C*).

GC-MS: R_t = 10.51 min; *m*/*z* (%) = 242 ($M^{\oplus}$, 10).

$C_{14}H_{10}O_4$: 242.23.

For the syntheses of the naphthalene-decorated *Fréchet*-dendrons, and for general procedures for the preparation of dendritic benzyl alcohols/bromides with naphthalene units, including compound **D2**, see ref. 23.

4,4′-Bis(2′-oxymethylnaphthyl)benzil (G0)



G0

4,4′-Dihydroxybenzil (210 mg; 0.86 mmol), 2-bromomethylnaphthalene (440 mg; (2.00 mmol), potassium carbonate (360 mg; 2.60 mmol) and [18]crown-6 (100 mg; 0.35 mmol) were dissolved in dry acetone (50 ml) and heated to reflux for 48 h. The precipitate was filtered off, washed with dichloromethane, and the solvent removed under reduced pressure. The residue was dissolved in dichloromethane, washed with water, sodium hydrogen carbonate-solution, and again with water. The organic phase was dried with Na_2SO_4 and the solvent removed under reduced pressure. Purification by column chromatography (SiO_2; dichloromethane) yielded a yellowish solid (180 mg).

TLC (SiO_2): R_f = 0.6 (dichloromethane).

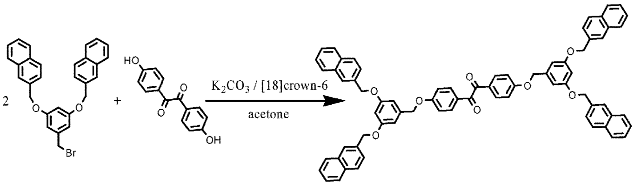
^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ [ppm] 5.31 (s, 4H, C*H*$_2$O), 7.08 (AA‘BB’, 4H, $^3J_{HH}$ = 9.04 Hz), 7.47–7.53 (m, 6H, naph-*H*), 7.82–7.89 (m, 8H, naph-*H*), 7.95 (AA‘BB’, 4H, $^3J_{HH}$ = 9.04 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ [ppm] 70.48 (*C*H$_2$O), 115.20, 125.01, 126.34, 126.44, 126.51, 126.57, 127.78, 127.95, 128.64, 132.40, 133.21, 133.26, 133.31, 163.00 (C_{ar}), 193.38 (ketone-*C*).

FAB-MS: *m*-NBA, *m*/*z* (%) = 523.2 (M + $H^{\oplus}$, 40).

$C_{27}H_{22}O_3$: 522.59.

4,4′-Bis[3,5-bis(2′-oxymethylnaphthyl)benzyloxy]benzil (G1)



G1

The experimental procedure is analogous to the synthesis of **G0**.

Scale: 4,4′-Dihydroxybenzil **50** (400 mg; 1.48 mmol), 3,5-bis(2′-oxymethylnaphthyl)benzyl bromide (1.5 g; 3.11 mmol), potassium carbonate (620 mg; 4.44 mmol) and [18]crown-6 (120 mg; 0.45 mmol) in dry acetone (150 ml). Purification by column chromatography (SiO_2; dichloromethane) yielded a yellowish solid (820 mg; 53%).

TLC (SiO_2): R_f = 0.6 (dichloromethane).

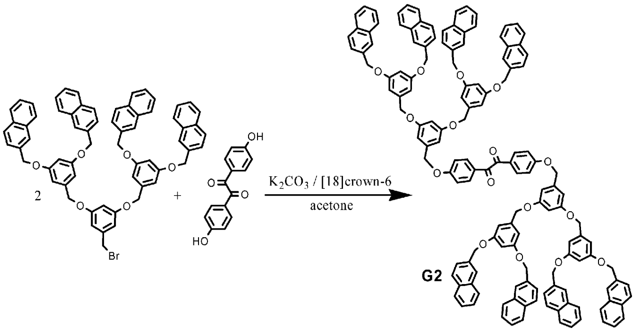
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 5.07 (s, 4H, ar-C*H*$_2$O), 5.20 (s, 8H, naph-C*H*$_2$O), 6.68 (t, 2H, $^4J_{HH}$ = 2.2 Hz, ar-*H*), 6.70 (d, 4H, $^4J_{HH}$ = 2.2 Hz, ar-*H*), 6.98 (AA‘BB’, 4H, $^4J_{HH}$ = 9.0 Hz), 7.46–7.52 (m, 12H, naph-*H*), 7.81–7.86 (m, 16H, naph-*H*) 7.90 (AA‘BB’, 4H, $^4J_{HH}$ = 9.0 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ [ppm] 70.17, 70.36 (*C*H$_2$O), 102.03, 106.50, 115.19, 125.25, 126.15, 126.30, 126.40, 126.58, 127.77, 127.96, 128.46, 132.36, 133.13, 133.32, 133.18, 138.40, 160.35, 163.84 (C_{ar}), 194.38 (ketone-*C*).

FAB-MS: *m*-NBA, *m*/*z* (%) = 1047.5 (M + $H^{\oplus}$, 10).

$C_{72}H_{54}O_8$: 1047.19.

4,4′-Bis[3,5-bis[3′,5′-bis(2″-oxymethylnaphthyl)-benzyloxy]benzyloxy]benzil (G2)



The experimental procedure is analogous to the synthesis of **G0**.

Scale: 4,4′-Dihydroxybenzil (91.5 mg; 0.38 mmol), 3,5-bis[3′,5′-bis(2″-oxymethylnaphthyl)benzyloxy]benzyl bromide (800 mg; 0.79 mmol), potassium carbonate (260 mg; 1.90 mmol) and [18]crown-6 (40 mg; 0.15 mmol) in dry acetone (80 ml). Purification by column chromatography (SiO_2; dichloromethane) yielded a yellowish solid (260 mg; 33%).

TLC (SiO_2): $R_f = 0.6$ (dichloromethane).

^1H NMR (400 MHz, $CDCl_3$, 25 °C): δ [ppm] 4.96 (s, 12H, Ar-C*H*$_2$O-Ar), 5.17 (s, 16H, naph-C*H*$_2$O-ar), 6.55 (t, 2H, $^4J_{HH}$ = 2.3 Hz, Ar-*H*), 6.59 (d, 4H, $^4J_{HH}$ = 2.3 Hz, ar-*H*), 6.65 (t, 4H, $^4J_{HH}$ = 2.2 Hz, Ar-*H*), 6.71 (d, 8H, $^4J_{HH}$ = 2.2 Hz, Ar-*H*), 6.96 (AA'BB', 4H, $^3J_{HH}$ = 9.0 Hz), 7.44–7.50 (m, 24H, naph-*H*), 7.78–7.84 (m, 32H, naph-*H*) 7.90 (AA'B', 4H, $^3J_{HH}$ = 9.0 Hz).

^{13}C NMR (100.6 MHz, $CDCl_3$, 25 °C): δ [ppm] 70.05, 70.12, 70.29 (*C*H$_2$O), 101.80, 101.85, 106.43, 106.53, 115.16, 125.29, 126.09, 126.25, 126.38, 126.56, 127.75, 127.97, 128.41, 132.37, 133.11, 133.32, 134.28, 138.29, 139.24, 160.17, 160.27, 163.85 (C_{ar}), 193.37 (ketone-*C*).

MALDI-TOF-MS: Matrix: DHB; m/z (%) = 2119.6 ($[M + Na]^{\oplus}$, 100)

$C_{143}H_{110}O_{16}$: 2096.40.

Photophysical and photochemical experiments

The experiments were performed in dichloromethane–chloroform 1 : 1 (v/v) mixture, unless otherwise noted. Deaerated solutions were obtained by three freeze–pump–thaw cycles.

UV-Vis absorption spectra were recorded with a Perkin Elmer λ40 spectrophotometer, using quartz cells with path-length of 1.0 cm. Emission spectra and phosphorescence lifetimes were obtained with a Perkin Elmer LS-50 spectrofluorimeter, equipped with a Hamamatsu R928 phototube. Fluorescence quantum yields were measured following the method of Demas and Crosby[24] (standard used: naphthalene, $\Phi = 0.23$ in deaerated cyclohexane).[25] Prompt fluorescence lifetimes were measured by time-correlated single-photon counting (0.5 ns time resolution) by an Edinburgh Instrument equipped with a TCC900 card and a D_2 lamp. Nanosecond transient absorption experiments were performed in argon purged acetonitrile solutions. A Continuum Surelite SLI-10 Nd:YAG laser was used to excite the sample with 10-ns pulses at 355 nm. The monitoring beam was supplied by a Xe arc lamp, and the signal was detected by a red sensitive photodiode after passing through a high radiance monochromator. Differential absorption spectra were recorded point-by-point, while kinetic measurements were made at fixed wavelength. 32 individual laser shots were averaged to improve the reliability of each acquisition. Transient absorption decays were fitted by considering both a first- (intrinsic deactivation) and a second-order (triplet-triplet annihilation) component, according to the following equations:

$$-\frac{d[^*A]}{dt} = k[^*A] + k'[^*A]^2 \Rightarrow [^*A] = \frac{[^*A]_0 k}{([^*A]_0 k' + k)e^{kt} - [^*A]_0 k'}$$

where $[^*A]_0$ is the concentration of excited state (*A) at zero time, when the laser pulse of excitation is switched on, k and k' are the rate constants of the first- and second-order processes, respectively.

Continuous irradiation experiments were performed by a medium pressure mercury lamp. An interference filter (Oriel) was used to select a narrow spectral range with λ_{max} = 313 nm. The irradiated solution (3 ml, 2×10^{-5} M) was contained in a spectrophotometric cell. The intensity of the incident light (8.3×10^{-8} einstein min^{-1} at 313 nm), measured by the ferrioxalate actinometer,[26] was the same in all experiments.

The estimated experimental errors are: ±2 nm on the band maximum, 5% on the molar absorption coefficient, 10% on the fluorescence and photoreaction quantum yield, 5% on the lifetime.

Electrochemical and spectroelectrochemical measurements. Electrochemical experiments were carried out in argon-purged CH_2Cl_2 (Romil Hi-Dry™) solutions at room temperature with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm^2, Amel); the counter electrode was a Pt spiral and a silver wire was employed as a quasi-reference electrode (QRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene (+0.46 V *vs.* SCE). The concentration of the compounds examined was of the order of 5×10^{-4} M; 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) was added as supporting electrolyte. Cyclic voltammograms were obtained with scan rates in the range 0.05–5 V s^{-1}. The number of electrons exchanged in each process was estimated by comparing the current intensity of the corresponding CV wave with that observed for the monoelectronic oxidation of ferrocene, after correction for differences in the diffusion coefficients. The experimental error on the potential values was estimated to be ±10 mV.

Spectroelectrochemical experiments were performed in an optically transparent thin layer electrode (OTTLE) cell constituted by two quartz windows, a three-electrode set melt-sealed in a polyethylene spacer. The three electrodes are: two Pt minigrids (32 wires cm^{-1}) as working and counter electrodes and a silver wire as quasi-reference electrode, positioned very close to the working electrode to minimize Ohmic resistance. The cell has a sandwich type arrangement. The light is passed through the central part of the working electrode minigrid (*ca.* 80% transmittance) and the light path is of the order of 100–200 μm. Diffusion of electrogenerated species between the electrodes is negligible on the experimental time scale (10–50 s). The solution used for spectroelectrochemical experiments was prepared as previously described for cyclic voltammetry. In order to localize the right potential window corresponding to the redox process of interest, a thin layer cyclic voltammetry (TLCV) was recorded at 5 mV s^{-1} before the spectroelectrochemistry. After refilling the OTTLE cell with new solution, the electrolysis potential was varied with 20–50 mV steps and UV-VIS-NIR absorption spectra were recorded with an Agilent Technologies 8543 diode array spectrophotometer.

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