Fullerene-rich dendrimers: divergent synthesis and photophysical properties†

Uwe Hahn,‡[a] Jean-François Nierengarten,*[a] Fritz Vögtle,*[b] Andrea Listorti,[c] Filippo Monti[c] and Nicola Armaroli*[c]

Received (in Montpellier, France) 18th September 2008, Accepted 31st October 2008
First published as an Advance Article on the web 19th December 2008
DOI: 10.1039/b816336g

Dendrimers containing up to 16 fullerene peripheral subunits have been prepared by a divergent synthetic approach based on the functionalization of polypropyleneimine (PPI) dendrimers with a C_{60} derivative bearing an activated carboxylic acid function. The absorption and fluorescence properties of these compounds are substantially identical in toluene and benzonitrile. Enhanced absorption in the region between 350 and 500 nm is detected by increasing the generation number, attributable to intramolecular interactions. A size-dependent trend of decreasing singlet lifetimes (−16%) and fluorescence quantum yields (−18%) is observed. The fullerene triplet state of the dendrimers was monitored *via* laser flash-photolysis in toluene and benzonitrile. In both media the transient absorption signal intensity is decreased with the molecular size and the effect is more pronounced in oxygen-free solution (−60%) compared to air-equilibrated samples (−37%). In toluene the triplet decay kinetics is unchanged for the whole series, ruling out the possibility of self-quenching effects, whereas in benzonitrile a triplet lifetime increase is recorded as a consequence of fullerene self-protection towards oxygen quenching. No amine→fullerene photoinduced electron transfer is detected because the complex molecular architecture does not allow the establishment of favourable donor–acceptor distances.

Introduction

Dendrimer chemistry and fullerenes cross each other to give rise to a new interdisciplinary field in which chemists have designed and prepared unprecedented fullerene-based nanoarchitectures.[1–3] Whereas dendrimers with a fullerene core have been studied to a large extent,[1,4] the synthesis of fullerene-rich dendrimers has been considered to a lesser degree. This is mainly associated with the difficulties encountered in their synthesis. The two major problems for the preparation of such dendrimers are the low solubility of C_{60} derivatives and their chemical reactivity, which limit the range of reactions that can be used for the synthesis of branched structures bearing multiple C_{60} units. Over the past years, we have developed efficient convergent methodologies allowing the preparation of dendrons substituted with several fullerene moieties.[2,5] These fullerodendrons are suitable building blocks for the preparation of large fullerene-rich dendritic molecules by using either covalent chemistry[6] or supramolecular interactions.[3,7] Substantial research efforts have also been carried out to organize such compounds onto surfaces[8] or to study their electronic properties.[9] Recently, it has been shown that dendrimers bearing multiple C_{60} units are good candidates for solar energy conversion.[10] Importantly, significant changes in the photoelectrochemical properties have been evidenced by increasing the generation number. In particular, the incident photon-to-photocurrent efficiency (IPCE) of the devices is significantly increased by increasing the generation number and thus the number of C_{60} subunits of the dendritic molecules used in the photoactive layer. The latter observation is a strong driving force to develop new efficient synthetic strategies for the preparation of large fullerene-rich dendritic molecules. In this paper, we describe the first divergent preparation of fullerene-rich dendrimers. The photophysical properties of these dendrimers bearing up to 16 fullerene moieties are also reported.

Results and discussion

Synthesis

The synthetic approach to prepare dendrimers **G0–G3** (Fig. 1) relies upon the activation of the carboxylic acid function of fullerene derivative **1**[11] followed by grafting onto the peripheral amine units of polypropyleneimine (PPI) dendrimers (Scheme 1). The choice of the appropriate activating group for the carboxylic

[a] *Laboratoire de Chimie des Matériaux Moléculaires, Ecole Européenne de Chimie, Polymères et Matériaux, Université Louis Pasteur et CNRS (UMR 7509), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France. E-mail: nierengarten@chimie.u-strasbg.fr; Fax: +33 390 242774; Tel: +33 390 242764*
[b] *Kekulé-Institut für Organische Chemie und Biochemie, Rheinische Friedrich-Wilhelms-Universität Bonn, Gerhard-Domagk-Strasse 1, 53121 Bonn, Germany. E-mail: voegtle@uni-bonn.de; Fax: +49 228 735662; Tel: +49 228 733496*
[c] *Molecular Photoscience Group, Istituto per la Sintesi Organica e la Fotoreattività, Consiglio Nazionale delle Ricerche, via Gobetti 101, 40129 Bologna, Italy. E-mail: nicola.armaroli@isof.cnr.it; Fax: +39 051 639 9844; Tel: +39 051 639 9820*
† Dedicated to Dr Jean-Pierre Sauvage on the occasion of his 65th birthday.
‡ Present address: Departamento de Química Orgánica, Facultad de Ciencias, Campus de Cantoblanco, Universidad Autónoma de Madrid, 28049 Madrid, Spain.

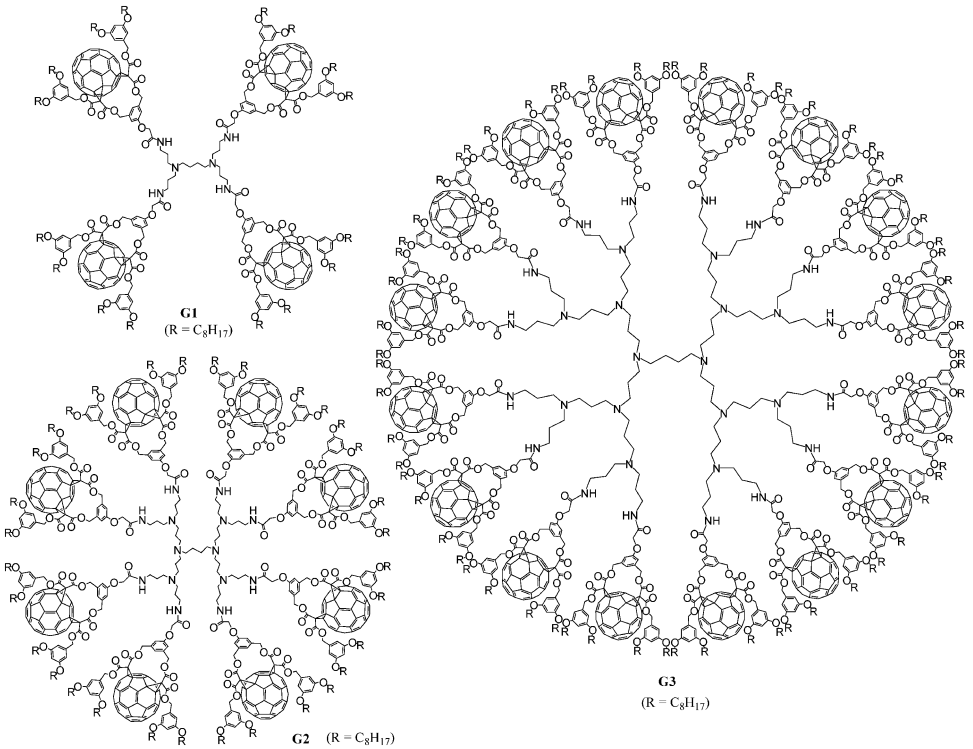
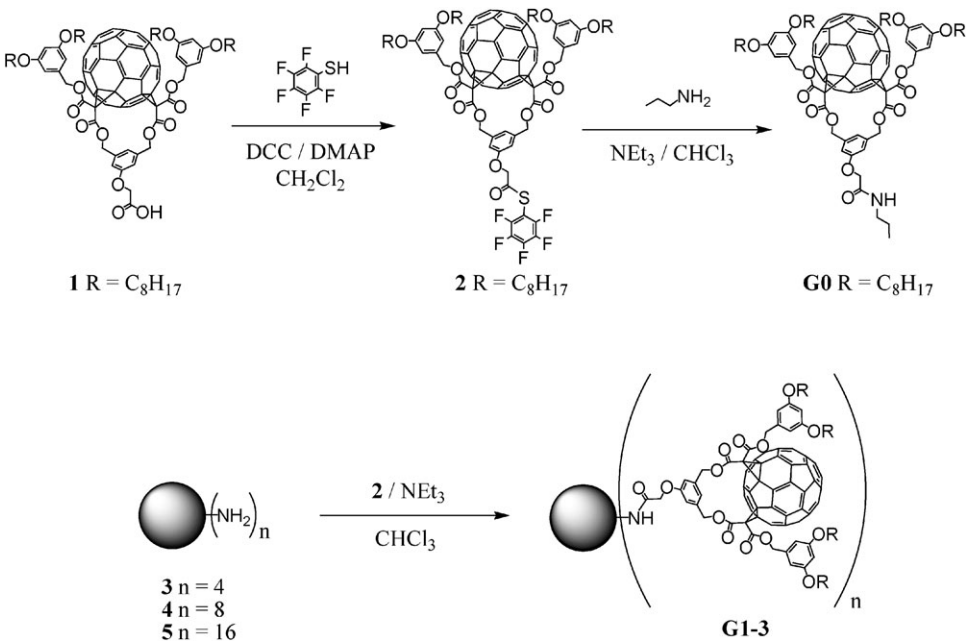


Fig. 1 Fullerene-rich dendrimers **G1–G3**.



Scheme 1 Preparation of **G0** (top) and **G1–G3** (bottom).

acid function of the C_{60} building block was the key to this synthesis. Effectively, the reaction conditions for the activation step can not be to strongly acid or basic, in order to preserve the ester functions. Furthermore, the grafting onto the dendritic polyamines requires an extremely efficient reaction to obtain the corresponding functionalized derivatives with good yields and to avoid the formation of defected dendrimers. The preparation of the pentafluorothiophenol ester **2** from compound **1** and pentafluorothiophenol under *N*,*N*′-dicyclohexylcarbodiimide (DCC)-mediated esterification conditions appeared as a good choice. Indeed, the reaction conditions for the preparation of **2** are mild and the efficient grafting of pentafluorothiophenol esters onto PPI dendrimers has already been reported.[12] Compound **2** was obtained in nearly quantitative yields by reaction of carboxylic acid **1** with pentathiofluorothiophenol in the presence of DCC and a catalytic amount of 4-dimethylaminopyridine (DMAP).

Subsequently, compound **2** was treated with propylamine in the presence of triethylamine to afford the corresponding propylamide reference compound **G0** in 74% isolated yield (Scheme 1). The reaction conditions were then applied to the functionalization of the PPI dendrimers **3–5**. Treatment of **3–5** with a slight excess of **2** (1.05 equiv. per terminal primary amine function) in the presence of triethylamine provided the dendritic derivatives **G1–G3** in moderate to high yields. The purification of the products was achieved by preparative gel permeation chromatography (GPC). In all cases, the dendrimers could be easily separated from the excess of **2**. Indeed, the purification of the highest generation compounds proved to be even easier due to the increased difference in molecular weights between the dendrimer and compound **2**.

Owing to the presence of four pendant alkyl chains per fullerene moiety, compounds **G0–G3** are all well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF or toluene, and spectroscopic characterization was easily achieved. The ^{1}H NMR spectra of dendrimers **G1–G3** show the typical pattern of the fullerene *cis*-2 bis-adduct with the expected additional signals arising from the PPI skeleton. The integration ratio are also consistent with the proposed molecular structures. It is worth mentioning that the ^{1}H NMR spectra of **G1–G3** recorded at room temperature are broad when compared to that recorded for **G0** under the same conditions. Indeed, the broadening becomes more important when the generation number is increased. Variable-temperature NMR studies ($C_2D_2Cl_4$, 300 MHz) showed a perfectly reversible narrowing of all the peaks and sharp spectra were obtained for **G1–G3** at 383 K. The latter observation can be ascribed to significant changes in the relaxation time *T*2 as a result of the large increase in molecular weight and/or to the slow dynamic exchange between *cis* and *trans* amide isomers at room temperature. Finally, the structure of **G0–2** was confirmed by MALDI-TOF mass spectrometry. The expected molecular ion peaks were clearly observed for all the compounds. It should be pointed out that no peaks corresponding to defected dendrimers were observed in the mass spectra of **G1–2**, thus providing clear evidence for their monodispersity. For **G3**, a high level of fragmentation prevented the observation of the expected molecular ion peak. As already described for related fullerene-rich dendrimers,[13] the fragmentation results from the hydrolysis of 3,5-dioctyloxybenzylic ester groups. This first process is generally followed by a decarboxylation reaction.

Absorption and fluorescence properties, singlet lifetimes

UV-Vis absorption and emission spectra of **G0–G3** were recorded in toluene and benzonitrile, two aromatic solvents of different polarity, but no substantial differences were found in the two cases. Fig. 2 shows the electronic absorption spectra of **G0–G3** in toluene; for comparison purposes, spectral traces of solutions having the same concentration of fullerene units, *i.e.* 0.05 mM, are reported. Almost featureless profiles are recorded at $\lambda > 300$ nm with two shoulders in the UV region around 330 and 370 nm and a weak band at about 430 nm; this pattern is typical for bis-functionalized methanofullerenes.[14] By increasing the dendrimer generation the absorption profiles

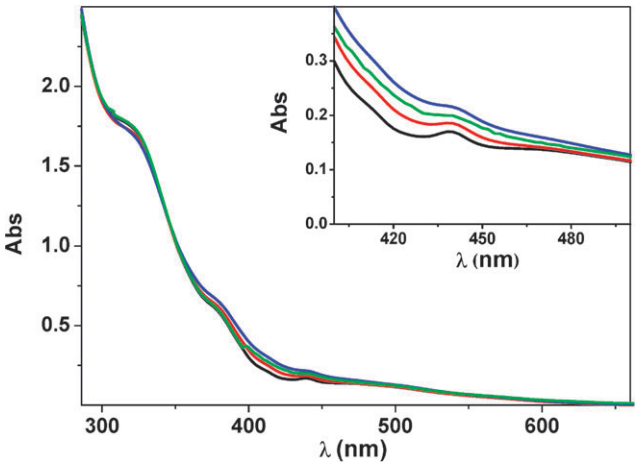


Fig. 2 Absorption spectra of **G0** (black), **G1** (red), **G2** (green), **G3** (blue) in toluene at 298 K ([C_{60}] = 0.05 mM). The spectral window between 400 and 500 nm is enlarged in the inset.

of **G0–G3** are only affected in the region between 350 and 500 nm, where some spectral widening is detected. A similar behaviour was observed for fullerene complex architectures, where the carbon sphere is in close contact with other molecular subunits, for instance fullerodendrimers,[14,15] compact hybrid systems with coordination compounds[16] and host–guest supramolecular adducts.[17] Light harvesting capability of **G1–G3** increases dramatically along the series: molar extinction coefficients of the largest dendrimer in the UV region exhibit values as high as 672 000 M^{-1} cm^{-1} at 300 nm (Table 1). The optical properties of solutions of **G0–G3** are stable for days even after laser irradiation (*vide infra*), suggesting a marked photostability.

The fluorescence spectra of **G0–G3** in toluene exhibit the typical shape of bismethanofullerenes (Fig. 3),[18] with maxima at 785 nm (spectra corrected for the instrumental response), unchanged with dendrimer generation. The emission quantum yields and singlet lifetimes for the whole series are reported in Table 1. Some intensity decrease is found when the dendrimer size is increased and also singlet lifetimes turn out to be shorter for larger dendrimers, going from 1.47 (**G0**) to 1.24 ns (**G3**). This trend was found for a similar family of fullerodendrimers with methanofullerene monoadducts[10] and is likely to be associated with some degree of intramolecular interaction among the carbon spheres, as also suggested by ground-state absorption spectra (see above).

Dendrimers containing amine groups can be protonated at the nitrogen lone pair, sometimes showing tuning of the photophysical properties as a consequence of intramolecular rearrangements.[19–21] We added up to ten equivalents of trifluoroacetic acid to **G1–G3** both in toluene and in benzonitrile, but no changes of the absorption ($\lambda > 300$ nm) and fluorescence properties were observed. These are exclusively attributable to the carbon spheres, which clearly do not perturb their own electronic levels following protonation, even if this process is most likely accompanied by structural rearrangements of the dendritic internal structure.[19]

Photoinduced electron transfer between C_{60} derivatives and aliphatic amines has been reported both in bimolecular processes (*i.e.* diffusion-controlled)[22,23] and in multicomponent

Table 1 Molar extinction coefficients for selected wavelengths, fluorescence maxima (values from corrected spectra in parentheses), singlet lifetimes and fluorescence quantum yields of **G0–G3** in toluene

	Absorption		Fluorescence		
	ε (330 nm)/M^{-1} cm^{-1}	ε (430 nm)/M^{-1} cm^{-1}	λ_{max}/nm	τ/ns	$10^{-4}\Phi$
G0	35 000	3500	709 (783)	1.47	2.8
G1	138 000	16 200	705 (784)	1.38	2.4
G2	282 000	35 400	705 (786)	1.27	2.2
G3	548 000	79 100	709 (785)	1.24	2.3

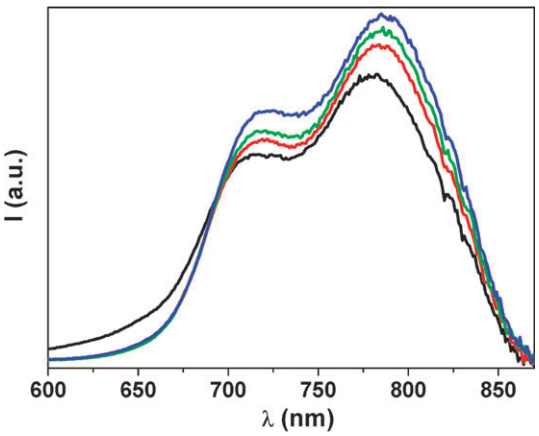


Fig. 3 Fluorescence spectra, corrected for the photomultiplier response, of **G0** (black), **G1** (red), **G2** (green), **G3** (blue) in toluene solution at 298 K, λ_{exc} = 330 nm.

architectures.[24,25] In the present case quenching of the fullerene singlet states of **G1–G3** is not detected in toluene and in more polar benzonitrile indicating that, from this level, intramolecular electron transfer from the core (amine donors) to the periphery (fullerene acceptors) does not take place.

Triplet transient absorption spectra and lifetimes

Light excitation of fullerene adducts quantitatively generates the short-lived lowest singlet state which undergoes intersystem crossing to the lowest triplet level with high yield ($\geq$80%).[26–28] For **G0–G3** the triplet state was monitored by means of laser flash-photolysis, which in all cases discloses the intense triplet–triplet transient absorption band, peaked at 720 nm, typical of bismethanofullerene adducts (Fig. 4).[9] By monitoring the signal decay at 720 nm, triplet lifetimes were measured in toluene and benzonitrile solutions under air-equilibrated and oxygen-free conditions (Table 2).

In both media the transient absorption signal intensity of **G0–G3** is decreased with the molecular size; a 60% reduction is recorded for the largest system **G3**. Such an unusual trend was recently found for a similar family of fullerodendrimers with methanofullerene monoadducts as peripheral units.[10] This was tentatively attributed to the presence of strong *intra*molecular and possibly *inter*molecular hydrophobic interactions between the carbon spheres, leading to the formation of fullerene aggregates characterized by reduced intersystem crossing yields. Indeed, reduction of singlet–triplet intersystem crossing efficiency has been reported earlier for C_{60} aggregates, due to enhanced relaxation of the singlet excited state,[29] which is also observed here to a small extent (see above). The previously proposed rationale[10] seems to be corroborated by the present results. In the earlier study fullerodendrimers with 8 and 16 terminal carbon spheres exhibited a decrease of the absorption intensity >95%, whereas in the present case the quenching is only 25 and 60%, respectively. This substantial difference could be related to a markedly decreased propensity of bismethanofullerene terminal units, compared to analogous monoadducts, to get in close contact and yield aggregates, owing to a larger steric hindrance. The reduced interaction among carbon spheres, particularly in apolar toluene, is confirmed by the invariance of the triplet lifetime along the series (Table 2), which also rules out the possibility of triplet self-quenching processes.[30–32] This finding is in line with other bismethanofullerene dendrimers[9] but differs from monomethane analogues where triplet lifetimes are decreased up to 6-fold.[10] Importantly, the unchanged value of the fullerene triplet lifetime of **G1–G3** compared to **G0**, also underpins the lack of photoinduced electron transfer from the amine groups to the peripheral carbon spheres upon excitation of the fullerene triplet.

Data in air-equilibrated solutions show that the triplet absorption signal intensity is still decreased with dendrimer size, but to a lesser extent compared to oxygen-free solutions (−37% for **G3**, Fig. 4). The fitted lifetimes are prolonged with dendrimer generation both in toluene and benzonitrile (Table 2). The trend of triplet lifetimes in air-equilibrated solutions is reminiscent of what was previously observed with fullerodendrimers having the carbon sphere as central core.[14,15] For such systems the (larger) prolongation of the C_{60} triplet lifetime was attributed to a protective effect of the external dendritic skeleton towards interactions with O_2. In the present fullerodendrimers, where the carbon spheres are the external units, the formation of fullerene aggregates (see above) induces a self-protective effect, which is amplified by the dendrimer size.[10] Under these conditions the excited carbon sphere is partially shielded by other C_{60} moieties, retarding the diffusion-controlled interaction with the O_2 quencher.[10] The effect is much more pronounced in benzonitrile where the lifetime increase (+70%) is substantially larger than in toluene (+20%), because in the more polar medium hydrophobic fullerene units are expected to be in tighter vicinity.[14,15] Notably, the intensity of the sensitized singlet oxygen luminescence spectra in the near-infrared region is decreased by about 30% from **G0** to **G3** in toluene (Fig. 3). This result is in reasonable agreement with the observed triplet loss (see above) and shows a less pronounced effect compared to monomethanofullerene analogues (−40%).[10] Such observation provides further support to a reduced interaction among carbon spheres for the present fullerodendrimers, which limits the protective effect towards oxygen quenching.

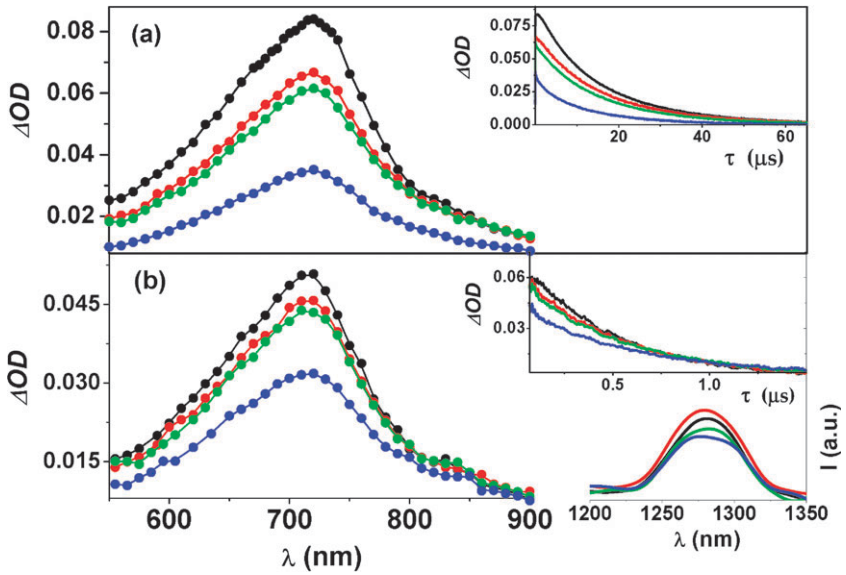


Fig. 4 Transient absorption spectra of **G0** (black), **G1** (red), **G2** (green), **G3** (blue) in oxygen-free (a) and air-equilibrated (b) toluene solutions; λ_{exc} = 532 nm, delay = 2 μs for (a) and 0.2 μs for (b), laser energy 0.3 mJ pulse^{-1}. Inset: transient absorption decay profiles at 720 nm. Bottom right panel in (b): singlet oxygen luminescence for **G0** (black), **G1** (red), **G2** (green), **G3** (blue) in air-equilibrated toluene solutions; λ_{exc} = 330 nm.

Table 2 Triplet lifetime data in toluene and benzonitrile, air-equilibrated and oxygen-free solutions. In order to avoid triplet–triplet annihilation processes and get monoexponential triplet decays, the laser excitation energy has to be kept lower than 0.3 mJ pulse^{-1}; λ_{exc} = 532 nm

	Toluene		Benzonitrile	
	Air eq. (ns)	O_2-free (μs)	Air eq. (ns)	O_2-free (μs)
G0	480	15	320	16.5
G1	520	16	440	15
G2	530	15	480	14
G3	570	14	580	10

Conclusions

We have presented for the first time the divergent preparation of fullerene-rich dendrimers. The photophysical properties of the complete series of compounds have been studied in detail. A size-dependent trend (**G0** → **G3**) of decreasing singlet lifetimes (−16%) and fluorescence relative intensities (−18%) is observed. The fullerene triplet state of **G0–G3** was monitored *via* laser flash-photolysis in toluene and benzonitrile. In both media the transient absorption signal intensity of **G0–G3** is decreased with the molecular size and the effect is more pronounced in oxygen-free solutions (−60%) compared to air-equilibrated samples (−37%). In deaerated conditions the triplet decay kinetics is unchanged for the whole series, ruling out the possibility of self-quenching effects, whereas in air-equilibrated samples a triplet lifetime increase is recorded as a consequence of fullerene self-protection towards oxygen quenching. The decrease of triplet formation for dendrimers **G0–G3**, that is confirmed by measurements of singlet oxygen sensitized luminescence in the NIR region, is attributed to the formation of *intra* and possibly *inter*-molecular aggregates among carbon spheres in solution. Solvent polarity effects and comparison with a previously studied family of fullerodendrimers, which showed an even more pronounced triplet depletion, bring support to this rationale. The lack of singlet or triplet quenching in fullerodendrimers **G1–G3**, shows that intramolecular electron transfer from the core to the periphery (amine→fullerene) does not take place, unlike several linear dyads or triads bearing the same molecular subunits reported to date. Evidently, in these complex molecular architectures structural constraints do not allow the establishment of suitable distances and electronic interactions between the donor–acceptor couples.

Experimental

Materials and methods

All reagents were used as purchased from commercial sources without further purification. Compound **1** was prepared according to a previously reported procedure.[11] Solvents were dried using standard techniques prior to use. All reactions were performed in standard glassware. Evaporation was done using a water aspirator and drying *in vacuo* at 10^{-2} Torr. Column chromatography: Merck silica gel 60, 40–63 μm (230–400 mesh). TLC: Precoated glass sheets with silica gel 60 F_{254} (Merck), visualization by UV light. Gel permeation chromatography was performed on Biorad, Biobeads SX-1 under the use of CH_2Cl_2 as eluent. UV/Vis spectra (λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1})) were measured on a Hitachi U-3000 spectrophotometer. IR spectra (cm^{-1}) were determined on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AM 300 (300 MHz) with solvent signal as reference. MALDI-TOF-MS were obtained on a Bruker BIFLEX™ mass spectrometer. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

Synthesis

Compound 2. DCC (193 mg, 0.93 mmol) was added to a stirred solution of **1** (1.12 g, 0.62 mmol), pentafluorothiophenol (0.12 mL, 0.93 mmol) and DMAP (30 mg, 0.25 mmol) in CH_2Cl_2 (30 ml) at 0 °C. The mixture was allowed to slowly warm to rt and then stirred for 1 d. Three drops of water were added, the solution stored at −20 °C for 30 min, filtered and evaporated. Column chromatography (SiO_2, CH_2Cl_2) yielded **2** (1.20 g, 98%) as a dark orange glassy product. IR (neat, cm^{-1}): 1750 (C═O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 6 Hz, 12 H), 1.27 (m, 40 H), 1.73 (m, 8 H), 3.86 (t, J = 6 Hz, 8 H), 4.86 (s, 2 H), 5.06 (d, J = 12 Hz, 2 H), 5.30 (AB, J = 12 Hz, 4 H), 5.78 (d, J = 12 Hz, 2 H), 6.37 (t, J = 2 Hz, 2 H), 6.48 (d, J = 2 Hz, 4 H), 6.90 (broad s, 2 H), 7.23 (broad s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.1, 22.7, 26.2, 29.3, 29.4, 31.8, 49.0, 66.9, 67.0, 68.2, 68.7, 70.6, 72.7, 101.6, 107.2, 113.0, 117.4, 134.3, 136.6, 139.0, 141.1, 141.2, 143.2, 143.6, 143.8, 144.0, 144.2, 144.3, 144.6, 145.0, 145.1, 145.2, 145.4, 145.6, 145.7, 145.8, 147.5, 148.6, 160.4, 162.5, 162.6, 191.5. Anal. Calc. for $C_{128}H_{87}F_5O_{14}S$: C 77.80, H 4.44. Found: C 77.77, H 4.35%.

General procedure for the preparation of G0–G3. To a solution of the appropriate amine and triethylamine (1.05 equiv. per terminal amine group) in chloroform was added **2** (1.05 equiv. per amine group) and stirred at rt for several days (**G0**: 2 d, **G1**: 4 d, **G2**: 5 d, **G3**: 6 d). The resulting solid was filtered off, the solvent evaporated and the crude product purified as outlined in the following.

Compound G0. Prepared from propylamine and purified by column chromatography (SiO_2, CH_2Cl_2) to give **G0** in 74% yield as a dark orange glassy product. IR (neat, cm^{-1}): 1750, 1671 (C═O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, J = 6 Hz, 12 H), 0.95 (t, J = 7 Hz, 2 H), 1.27 (m, 40 H), 1.60 (m, 2 H), 1.73 (m, 8 H), 3.33 (m, 2 H), 3.88 (t, J = 6 Hz, 8 H), 4.55 (s, 2 H), 5.02 (d, J = 12 Hz, 2 H), 5.28 (AB, J = 12 Hz, 4 H), 5.70 (d, J = 12 Hz, 2 H), 6.39 (t, J = 2 Hz, 2 H), 6.48 (d, J = 2 Hz, 4 H), 6.54 (t, J = 5 Hz, 1 H), 6.82 (s, 2 H), 7.21 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 11.5, 14.3, 22.8, 23.0, 26.2, 29.4, 29.5, 31.9, 40.9, 49.1, 67.0, 67.2, 67.7, 68.3, 68.9, 70.7, 101.8, 107.3, 112.7, 116.7, 134.4, 135.9, 136.2, 136.8, 138.0, 139.0, 140.1, 141.2, 141.3, 142.4, 142.9, 143.3, 143.7, 143.9, 144.1, 144.3, 144.4, 144.8, 145.1, 145.2, 145.3, 145.5, 145.8, 145.85, 145.9, 146.2, 147.5, 147.6, 157.4, 160.6, 162.7, 167.7. MALDI-TOF-MS: calc. for $C_{125}H_{95}NO_{14}$ m/z = 1835.13, found: 1835.4. Anal. Calc. for $C_{125}H_{95}NO_{14}$: C 81.81, H 5.22, N 0.76. Found: C 81.52, H 5.18, N 0.80%.

Compound G1. Prepared from **3** and purified by preparative size exclusion chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **G1** in 61% yield as a dark orange glassy product. IR (neat, cm^{-1}): 1750, 1674 (C═O). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.89 (t, J = 7 Hz, 48 H), 1.16–1.50 (m, 164 H), 1.72 (m, 40 H), 2.42 (br s, 8 H), 2.68 (br s, 4 H), 3.39 (br s, 8 H), 3.82 (t, J = 6 Hz, 32 H), 4.50 (s, 8 H), 5.10 (d, J = 12 Hz, 8 H), 5.27 (AB, J = 12 Hz, 16 H), 5.70 (d, J = 12 Hz, 8 H), 6.32 (s, 8 H), 6.45 (s, 16 H), 6.80 (br s, 8 H), 7.12 (s, 4 H), 7.30 (br s, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ 14.2, 22.7, 26.1, 28.0 (br), 29.3, 29.4, 31.0 (br), 31.9, 41.0 (br), 49.0, 51.0 (br), 54.0 (br), 66.8, 67.1, 68.1, 68.8, 70.6, 101.6, 107.2, 112.2, 115.6, 134.3, 135.7, 136.0, 136.5, 137.7, 138.8, 139.9, 141.1, 141.2, 142.1, 142.6, 143.2, 143.5, 143.7, 143.9, 144.17, 144.22, 144.6, 144.9, 145.0, 145.2, 145.3, 145.6, 145.68, 145.72, 146.0, 147.3, 147.5, 148.6, 157.4, 160.4, 162.5, 162.6, 168.2 (br). MALDI-TOF-MS: calc. for $C_{504}H_{384}N_6O_{56}$ m/z = 7420.60, found: 7420.4. Anal. Calc. for $C_{504}H_{384}N_6O_{56}{\cdot}3CH_2Cl_2$ C 79.34, H 5.12, N 1.09. Found: C 79.41, H 5.06, N 1.05%.

Compound G2. Prepared from **4** and purified by preparative size exclusion chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **G2** in 81% yield as a dark orange glassy product. IR (neat, cm^{-1}): 1749, 1672 (C═O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (t, ^3J = 7 Hz, 96 H), 1.16–1.50 (m, 324 H), 1.72 (m, 88 H), 2.42 (br s, 16 H), 2.68 (br s, 20 H), 3.39 (br s, 16 H), 3.82 (t, ^3J = 6 Hz, 64 H), 4.50 (s, 16 H), 5.10 (d, ^2J = 12 Hz, 16 H), 5.27 (AB, ^2J = 12 Hz, 32 H), 5.70 (d, ^2J = 12 Hz, 16 H), 6.32 (s, 16 H), 6.45 (s, 32 H), 6.80 (br s, 16 H), 7.12 (s, 8 H), 7.30 (br s, 8 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.6, 23.1, 26.6, 26.8, 26.9, 27.0 (br), 29.7, 29.8, 31.0 (br), 32.3, 37.8, 38.0 (br), 49.4, 49.5, 51.9, 52.0 (br), 54.0 (br), 67.2, 67.5, 67.8, 67.9, 68.5, 69.2, 71.0, 102.1, 107.6, 112.6, 116.0, 134.7, 136.1, 136.4, 136.9, 138.1, 139.2, 140.3, 141.5, 141.6, 142.6, 143.1, 143.6, 143.9, 144.1, 144.3, 144.6, 145.0, 145.3, 145.4, 145.6, 145.7, 145.8, 146.0, 146.1, 146.4, 147.7, 147.8, 149.0, 157.8, 160.8, 162.9, 163.0, 168.2 (br). MALDI-TOF-MS: calc. for $C_{1016}H_{784}N_{14}O_{112}$ m/z = 14981.43, found: m/z = 14980.9. Anal. Calc. for $C_{1016}H_{784}N_{14}O_{112}{\cdot}6CH_2Cl_2$ C 79.24, H 5.18, N 1.27. Found: C 79.01, H 5.13, N 1.15%.

Compound G3. Prepared from **5** and purified by preparative size exclusion chromatography (Biorad, Biobeads SX-1, CH_2Cl_2) to give **G3** in 52% yield as a dark orange glassy product. IR (neat, cm^{-1}): 1749, 1673 (C═O). ^1H NMR (300 MHz, $CDCl_3$): δ 0.89 (s, 198 H), 1.05–.48 (m, 644 H), 1.68 (m, 184 H), 2.00 (br s, 32 H), 2.40–3.30 (br s, 52 H), 3.39 (br s, 32 H), 3.77 (br s, 128 H), 4.50 (br s, 32 H), 5.05–.45 (br m, 96 H), 5.70 (br s, 32 H), 6.25 (s, 32 H), 6.40 (s, 64 H), 6.87 (br s, 32 H), 7.08 (s, 16 H), 7.60-7.95 (br s, 16 H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.2, 22.7, 26.2, 28.0 (br), 29.3, 29.5, 31.0 (br), 31.9, 37.0 (br), 49.1, 51.0 (br), 66.9, 67.1, 67.2, 68.0, 68.9, 70.7, 101.7, 107.2, 112.1, 134.4, 135.6, 135.9, 136.5, 137.9, 138.7, 139.9, 141.1, 142.1, 142.6, 143.1, 143.5, 143.6, 143.9, 144.1, 144.6, 144.9, 145.0, 145.1, 145.2, 145.6, 145.7, 146.0, 147.3, 147.4, 148.7, 157.6, 160.4, 162.6, 162.7, 168.7 (br). Anal. Calc. for $C_{2040}H_{1584}N_{30}O_{224}{\cdot}2CH_2Cl_2$: C 81.21, H 5.29, N 1.39. Found: C 81.01, H 5.23, N 1.45%.

Photophysics. Absorption spectra were recorded with a Perkin-Elmer λ40 spectrophotometer. Emission spectra were obtained with an Edinburgh FLS920 spectrometer (continuous 450 W Xe lamp), equipped with a Peltier-cooled Hamamatsu R928 photomultiplier tube (185–850 nm) or a Hamamatsu R5509-72 supercooled photomultiplier tube (193 K, 800–700 nm range). Emission quantum yields were determined according to the approach described by Demas and Crosby[33] using $[Ru(bpy)_3Cl_2]$ (λ_{em} = 0.028 in air-equilibrated water solution)[34] as standard.

Emission lifetimes were determined with the time correlated single photon counting technique using an Edinburgh FLS920 spectrometer equipped with a laser diode head as excitation source (1 MHz repetition rate, λ_{exc} = 407 nm, 200 ps time resolution upon deconvolution) and an Hamamatsu R928 PMT as detector. Transient absorption spectra in the nanosecond-microsecond time domain were obtained by using the nanosecond flash photolysis apparatus Proteus by Ultrafast Systems LLC, that was described in detail previously.[11] The samples were placed in fluorimetric 1 cm path cuvettes and, when necessary, purged from oxygen by at least four freeze–thaw–pump cycles. Typical laser power has been taken as 0.3 mJ pulse^{-1} which, taking into account the photon energy at 355 nm, the concentration of the sample, and the volume of solution effectively excited leads to an excitation of about 10% of the overall fullerene molecules, thus making negligible the chance of multiple excitation events within dendrimers. All measurements were carried out in spectroscopy grade toluene and benzonitrile, used without further purification. Experimental uncertainties are estimated to be 8% for lifetime determinations, 20% for emission quantum yields, 5% for relative emission intensities in the NIR, 1 nm and 5 nm for absorption and emission peaks, respectively.

Acknowledgements

This research was supported by the CNRS and CNR (Commessa PM.P04.010, MACOL). The German Academic Exchange Service (DAAD) is gratefully acknowledged for a post-doctoral fellowship to U. H.

References

1 (*a*) A. Hirsch and O. Vostrowsky, *Top. Curr. Chem.*, 2001, **217**, 51; (*b*) J.-F. Nierengarten, *New J. Chem.*, 2004, **28**, 1177; (*c*) J.-F. Nierengarten, N. Armaroli, G. Accorsi, Y. Rio and J.-F. Eckert, *Chem.–Eur. J.*, 2003, **9**, 36; (*d*) T. Chuard and R. Deschenaux, *J. Mater. Chem.*, 2002, **12**, 1944; (*e*) J.-F. Nierengarten, M. Guttiérez-Nava, S. Zhang, P. Masson, L. Oswald, C. Bourgogne, Y. Rio, G. Accorsi, N. Armaroli and S. Setayesh, *Carbon*, 2004, **42**, 1077; (*f*) N. Martin, *Chem. Commun.*, 2006, 2093; (*g*) N. Martin, L. Sanchez, M. A. Herranz, B. Illescas and D. M. Guldi, *Acc. Chem. Res.*, 2007, **40**, 1015; (*h*) D. Bonifazi, A. Kiebele, M. Stohr, F. Y. Cheng, T. Jung, F. Diederich and H. Spillmann, *Adv. Funct. Mater.*, 2007, **17**, 1051.

2 (*a*) J.-F. Nierengarten, *Chem.–Eur. J.*, 2000, **6**, 3667; (*b*) J.-F. Nierengarten, *Top. Curr. Chem.*, 2003, **228**, 87.

3 (*a*) U. Hahn, F. Cardinali and J.-F. Nierengarten, *New J. Chem.*, 2007, **31**, 1128; (*b*) T. M. Figueira-Duarte, A. Gégout and J.-F. Nierengarten, *Chem. Commun.*, 2007, 109; (*c*) J.-F. Nierengarten, U. Hahn, T. M. Figueira Duarte, F. Cardinali, N. Solladié, M. E. Walther, A. Van Dorsselaer, H. Herschbach, E. Leize, A.-M. Albrecht-Gary, A. Trabolsi and M. Elhabiri, *C. R. Chim.*, 2006, **9**, 1022.

4 (*a*) K. L. Wooley, C. J. Hawker, J. M. J. Fréchet, F. Wudl, G. Srdanov, S. Shi, C. Li and M. Kao, *J. Am. Chem. Soc.*, 1993, **115**, 9836; (*b*) C. J. Hawker, K. L. Wooley and J. M. J. Fréchet, *J. Chem. Soc., Chem. Commun.*, 1994, 925; (*c*) J.-F. Nierengarten, T. Habicher, R. Kessinger, F. Cardullo, F. Diederich, V. Gramlich, J.-P. Gisselbrecht, C. Boudon and M. Gross, *Helv. Chim. Acta*, 1997, **80**, 2238; (*d*) M. Brettreich and A. Hirsch, *Tetrahedron Lett.*, 1998, **39**, 2731; (*e*) Y. Rio, J.-F. Nicoud, J.-L. Rehspringer and J.-F. Nierengarten, *Tetrahedron Lett.*, 2000, **41**, 10207; (*f*) X. Camps and A. Hirsch, *J. Chem. Soc., Perkin Trans. 1*, 1997, 1595; (*g*) X. Camps, H. Schönberger and A. Hirsch, *Chem.–Eur. J.*, 1997, **3**, 561; (*h*) A. Herzog, A. Hirsch and O. Vostrowsky, *Eur. J. Org. Chem.*, 2000, 171; (*i*) N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud and J.-F. Nierengarten, *Chem. Commun.*, 2000, 599; (*j*) J. L. Segura, R. Gomez, N. Martin, C. P. Luo, A. Swartz and D. M. Guldi, *Chem. Commun.*, 2001, 707; (*k*) G. Accorsi, N. Armaroli, J.-F. Eckert and J.-F. Nierengarten, *Tetrahedron Lett.*, 2002, **43**, 65; (*l*) F. Langa, M. J. Gómez-Escalonilla, E. Díez-Barra, J. C. García-Martínez, A. de la Hoz, J. Rodríguez-López, A. González-Cortés and V. López-Arza, *Tetrahedron Lett.*, 2001, **42**, 3435; (*m*) D. M. Guldi, A. Swartz, C. Luo, R. Gomez, J. L. Segura and N. Martin, *J. Am. Chem. Soc.*, 2002, **124**, 10875; (*n*) L. Pérez, J. C. Garcia-Martinez, E. Diez-Barra, P. Atienzar, H. Garcia, J. Rodriguez-Lopez and F. Langa, *Chem.–Eur. J.*, 2006, **12**, 5149; (*o*) N. Armaroli, G. Accorsi, J. N. Clifford, J.-F. Eckert and J.-F. Nierengarten, *Chem.–Asian J.*, 2006, **1**, 564.

5 (*a*) J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 1999, **40**, 269; (*b*) J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 2000, **41**, 41; (*c*) D. Felder, H. Nierengarten, J.-P. Gisselbrecht, C. Boudon, E. Leize, J.-F. Nicoud, M. Gross, A. Van Dorsselaer and J.-F. Nierengarten, *New J. Chem.*, 2000, **24**, 687–695; (*d*) U. Hahn, K. Hosomizu, H. Imahori and J.-F. Nierengarten, *Eur. J. Org. Chem.*, 2006, 85.

6 U. Hahn, E. Maisonhaute, C. Amatore and J.-F. Nierengarten, *Angew. Chem., Int. Ed.*, 2007, **46**, 951.

7 (*a*) J.-F. Nierengarten, D. Felder and J.-F. Nicoud, *Tetrahedron Lett.*, 1999, **40**, 273; (*b*) J. Ruiz, C. Pradet, F. Varret and D. Astruc, *Chem. Commun.*, 2002, 1108; (*c*) U. Hahn, J. J. González, E. Huerta, M. Segura, J.-F. Eckert, F. Cardinali, J. de Mendoza and J.-F. Nierengarten, *Chem.–Eur. J.*, 2005, **11**, 6666; (*d*) J.-F. Nierengarten, U. Hahn, A. Trabolsi, H. Herschbach, F. Cardinali, M. Elhabiri, E. Leize, A. Van Dorsselaer and A.-M. Albrecht-Gary, *Chem.–Eur. J.*, 2006, **12**, 3365; (*e*) U. Hahn, A. Gégout, C. Duhayon, Y. Coppel, A. Saquet and J.-F. Nierengarten, *Chem. Commun.*, 2007, 516; (*f*) W.-S. Li, K. S. Kim, D.-L. Jiang, H. Tanaka, T. Kawai, J. H. Kwon, D. Kim and T. Aida, *J. Am. Chem. Soc.*, 2006, **128**, 10527; (*g*) R. van de Coevering, R. Kreiter, F. Cardinali, G. van Koten, J.-F. Nierengarten and R. J. M. Klein Gebbink, *Tetrahedron Lett.*, 2005, **46**, 3353; (*h*) B. Delavaux-Nicot, A. Kaeser, U. Hahn, A. Gégout, P.-E. Brandli, C. Duhayon, Y. Coppel, A. Saquet and J.-F. Nierengarten, *J. Mater. Chem.*, 2008, **18**, 1547.

8 (*a*) J.-F. Nierengarten, J.-F. Eckert, Y. Rio, M. P. Carreon, J.-L. Gallani and D. Guillon, *J. Am. Chem. Soc.*, 2001, **123**, 9743; (*b*) J. A. Camerano, M. A. Casado, U. Hahn, J.-F. Nierengarten, E. Maisonhaute and C. Amatore, *New J. Chem.*, 2007, **31**, 1395.

9 M. Gutiérrez-Nava, G. Accorsi, P. Masson, N. Armaroli and J.-F. Nierengarten, *Chem.–Eur. J.*, 2004, **10**, 5076.

10 K. Hosomizu, H. Imahori, U. Hahn, J.-F. Nierengarten, A. Listorti, N. Armaroli, T. Nemoto and S. Isoda, *J. Phys. Chem. C*, 2007, **111**, 2777.

11 D. Felder, M. Gutiérrez Nava, M. del Pilar Carreon, J.-F. Eckert, M. Luccisano, C. Schall, P. Masson, J.-L. Gallani, B. Heinrich, D. Guillon and J.-F. Nierengarten, *Helv. Chim. Acta*, 2002, **85**, 288.

12 (*a*) A. P. H. J. Schenning, C. Elissen-Román, J.-W. Weener, M. W. P. L. Baars, S. J. van der Gaast and E. W. Meijer, *J. Am. Chem. Soc.*, 1998, **120**, 8199; (*b*) M. W. P. L. Baars, S. H. M. Söntjens, H. M. Fischer, H. W. I. Peerlings and E. W. Meijer, *Chem.–Eur. J.*, 1998, **4**, 2456; (*c*) J. B. Christensen, M. F. Nielsen, J. A. E. H. Van Haare, M. W. L. P. Baars, R. A J. Janssen and E. W. Meijer, *Eur. J. Org. Chem.*, 2001, 2123; (*d*) A. Dirksen, U. Hahn, F. Schwanke, J. N. H. Reek, R. M. Williams, F. Vögtle and L. De Cola, *Chem.–Eur. J.*, 2004, **10**, 2036.

13 H. Herschbach, K. Hosomizu, U. Hahn, E. Leize, A. Van Dorsselaer, H. Imahori and J.-F. Nierengarten, *Anal. Bioanal. Chem.*, 2006, **386**, 46.

14 Y. Rio, G. Accorsi, H. Nierengarten, C. Bourgogne, J.-M. Strub, A. Van Dorsselaer, N. Armaroli and J.-F. Nierengarten, *Tetrahedron*, 2003, **59**, 3833.

15 Y. Rio, G. Accorsi, H. Nierengarten, J. L. Rehspringer, B. Honerlage, G. Kopitkovas, A. Chugreev, A. Van Dorsselaer, N. Armaroli and J. F. Nierengarten, *New J. Chem.*, 2002, **26**, 1146.

16 (*a*) Y. Rio, G. Enderlin, C. Bourgogne, J. F. Nierengarten, J. P. Gisselbrecht, M. Gross, G. Accorsi and N. Armaroli, *Inorg. Chem.*, 2003, **42**, 8783; (*b*) A. Listorti, G. Accorsi, Y. Rio, N. Armaroli, O. Moudam, A. Gégout, B. Delavaux-Nicot, M. Holler and J.-F. Nierengarten, *Inorg. Chem.*, 2008, **47**, 6254.
17 J. F. Eckert, D. Byrne, J. F. Nicoud, L. Oswald, J. F. Nierengarten, M. Numata, A. Ikeda, S. Shinkai and N. Armaroli, *New J. Chem.*, 2000, **24**, 749.
18 M. Holler, F. Cardinali, H. Mamlouk, J. F. Nierengarten, J. P. Gisselbrecht, M. Gross, Y. Rio, F. Barigelletti and N. Armaroli, *Tetrahedron*, 2006, **62**, 2060.
19 (*a*) C. Saudan, V. Balzani, P. Ceroni, M. Gorka, M. Maestri, V. Vicinelli and F. Vögtle, *Tetrahedron*, 2003, **59**, 3845; (*b*) U. Hahn, M. Gorka, F. Vögtle, V. Vicinelli, P. Ceroni, M. Maestri and V. Balzani, *Angew. Chem., Int. Ed.*, 2002, **41**, 3595.
20 G. Bergamini, P. Ceroni, V. Balzani, L. Cornelissen, J. van Heyst, S. K. Lee and F. Vögtle, *J. Mater. Chem.*, 2005, **15**, 2959.
21 B. Branchi, P. Ceroni, G. Bergamini, V. Balzani, M. Maestri, J. van Heyst, S. K. Lee, F. Luppertz and F. Vögtle, *Chem.–Eur. J.*, 2006, **12**, 8926.
22 M. Fujitsuka, C. P. Luo and O. Ito, *J. Phys. Chem. B*, 1999, **103**, 445.
23 A. S. D. Sandanayaka, Y. Araki, C. P. Luo, M. Fujitsuka and O. Ito, *Bull. Chem. Soc. Jpn.*, 2004, **77**, 1313.
24 A. S. D. Sandanayaka, H. Sasabe, Y. Araki, Y. Furusho, O. Ito and T. Takata, *J. Phys. Chem. A*, 2004, **108**, 5145.
25 M. E. El-Khouly, J. H. Kim, M. Kwak, C. S. Choi, O. Ito and K. Y. Kay, *Bull. Chem. Soc. Jpn.*, 2007, **80**, 2465.
26 R. V. Bensasson, E. Bienvenue, C. Fabre, J. M. Janot, E. J. Land, S. Leach, V. Leboulaire, A. Rassat, S. Roux and P. Seta, *Chem.–Eur. J.*, 1998, **4**, 270.
27 T. Hamano, K. Okuda, T. Mashino, M. Hirobe, K. Arakane, A. Ryu, S. Mashiko and T. Nagano, *Chem. Commun.*, 1997, 21.
28 F. Prat, R. Stackow, R. Bernstein, W. Y. Qian, Y. Rubin and C. S. Foote, *J. Phys. Chem. A*, 1999, **103**, 7230.
29 A. Quaranta, D. J. McGarvey, E. J. Land, M. Brettreich, S. Burghardt, H. Schonberger, A. Hirsch, N. Gharbi, F. Moussa, S. Leach, H. Gottinger and R. V. Bensasson, *Phys. Chem. Chem. Phys.*, 2003, **5**, 843.
30 S. Hashimoto, T. Miyashita and M. Hagiri, *J. Phys. Chem. B*, 1999, **103**, 9149.
31 H. T. Etheridge and R. B. Weisman, *J. Phys. Chem.*, 1995, **99**, 2782.
32 V. Ramesh, N. Ramnath and V. Ramamurthy, *J. Photochem.*, 1983, **23**, 141.
33 J. N. Demas and G. A. Crosby, *J. Phys. Chem.*, 1971, **75**, 991.
34 K. Nakamaru, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2697.

