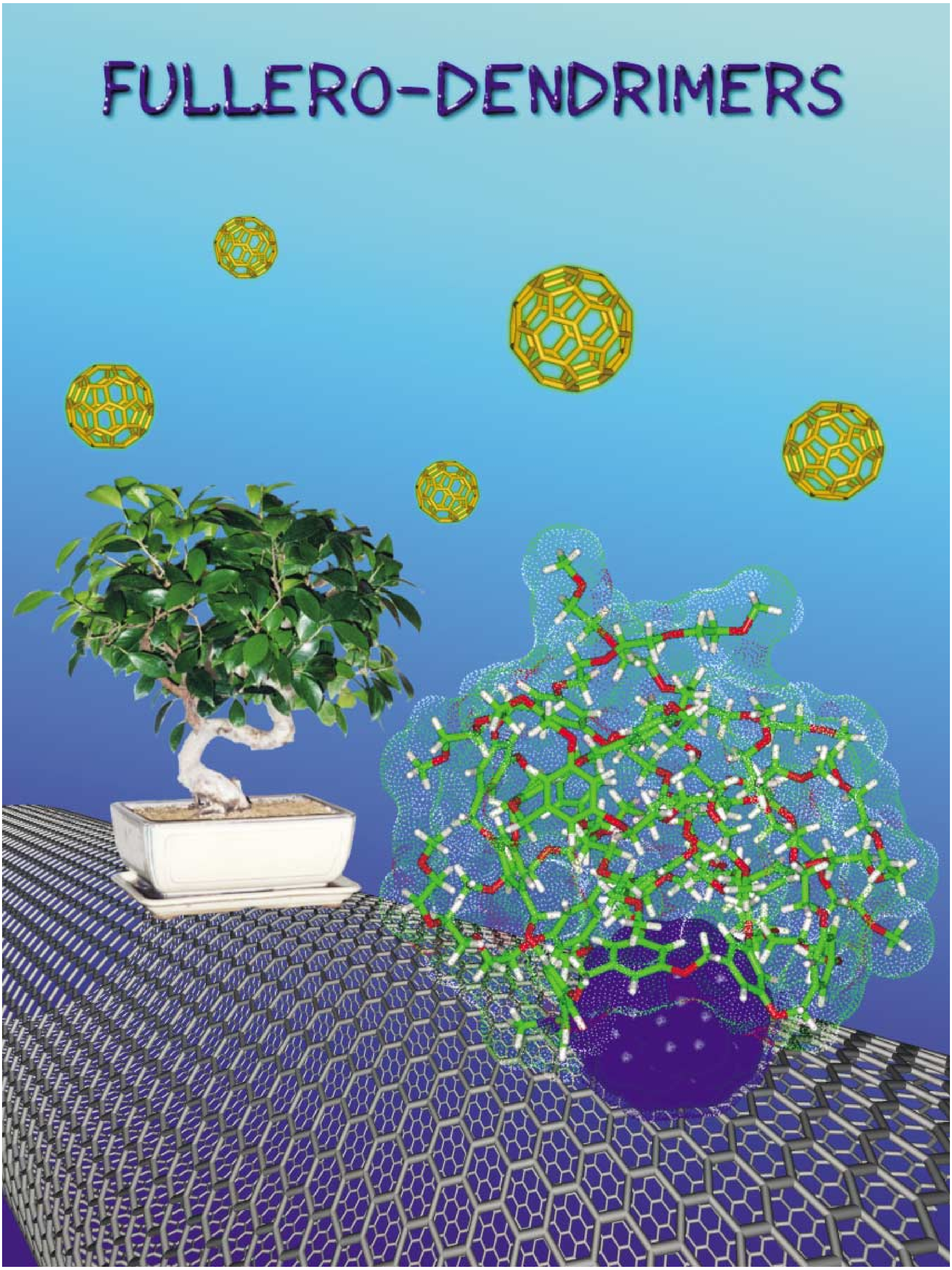
FULLERO-DENDRIMERS

[60]Fullerene: A Versatile Photoactive Core for Dendrimer Chemistry

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Abstract: Owing to their special photophysical properties, fullerene derivatives are good candidates to demonstrate dendritic effects. In particular, the triplet lifetimes of a C_{60} core can be used to evaluate its degree of isolation from external contacts. On the other hand, the fullerene core can act as a terminal energy receptor in dendrimer-based light-harvesting systems. When a fullerodendrimer is further functionalized with a suitable electron donor, it may exhibit the essential features of a multicomponent artificial photosynthetic system in which photoinduced energy transfer from the antenna to the C_{60} core is followed by electron transfer.

Keywords: dendrimers · electron transfer · energy transfer · fullerenes · materials science

Introduction

Dendrimers have attracted increased attention among various scientific communities in the last fifteen years.[1] This interest is mainly related to the capability of dendritic architectures to generate specific properties, as a result of their unique molecular structures. For example, a dendritic framework can surround active core molecules, thus creating specific site-isolated microenvironments capable of affecting the properties of the core itself.[2] The multiplication of functional groups at the periphery of a dendritic structure also provides several advantages. For example, the dendrimer surface can be used as a platform for amplification of substrate binding[3] or as an antenna for light-harvesting.[4] Furthermore dendrimers can be used as traps for small molecules or ions with the aim of releasing them where needed (e.g. in biological tissues)[5] or improving their properties (e.g. luminescence).[6]

Fullerenes possess electronic and photophysical properties[7] which make them natural candidates for the preparation of functional dendrimers.[8–10] In a previous concept article,[9] we have shown that C_{60} is a versatile building block for dendrimer chemistry. We have also highlighted specific advantages brought about by the encapsulation of a fullerene moiety in the middle of a dendritic structure for the preparation of thin ordered films or in the design of liquid crystalline derivatives.[9, 10] In the present paper, the use of the fullerene sphere as a photoactive core unit will be emphasized.

A Fullerene Core To Probe Dendritic Shielding Effects

Dendrimers with a fullerene core appear to be appealing candidates to demonstrate the shielding effects resulting from the presence of the surrounding dendritic shell.[11, 12] Effectively, the lifetime of the first triplet excited state of fullerene derivatives is sensitive to the solvent.[12] Therefore, lifetime measurements in different solvents can be used to evaluate the degree of isolation of the central C_{60} moiety from external contacts. With this idea in mind, we have prepared two series of fullerodendrimers (Figure 1).[12] In the design of these compounds, it was decided to attach poly(aryl ether) dendritic branches terminated with peripheral triethyleneglycol chains to obtain derivatives soluble in a wide range of solvents.[13] The synthetic approach to prepare compounds **1**–**4** relies upon the 1,3-dipolar cycloaddition[14] of the dendritic azomethine ylides generated in situ from the corresponding aldehydes and *N*-methylglycine. Dendrimers **5**–**8**[15] have been obtained by taking advantage of the versatile regioselective reaction developed in the group of Diederich,[16] which led to macrocyclic bis-adducts of C_{60} by a cyclization reaction at the C sphere with bis-malonate derivatives in a double Bingel cyclopropanation.[17]

The photophysical properties of **1**–**8** have been studied in different solvents (PhMe, CH_2Cl_2 and CH_3CN). The lifetimes of the lowest triplet excited states are summarized in Table 1.

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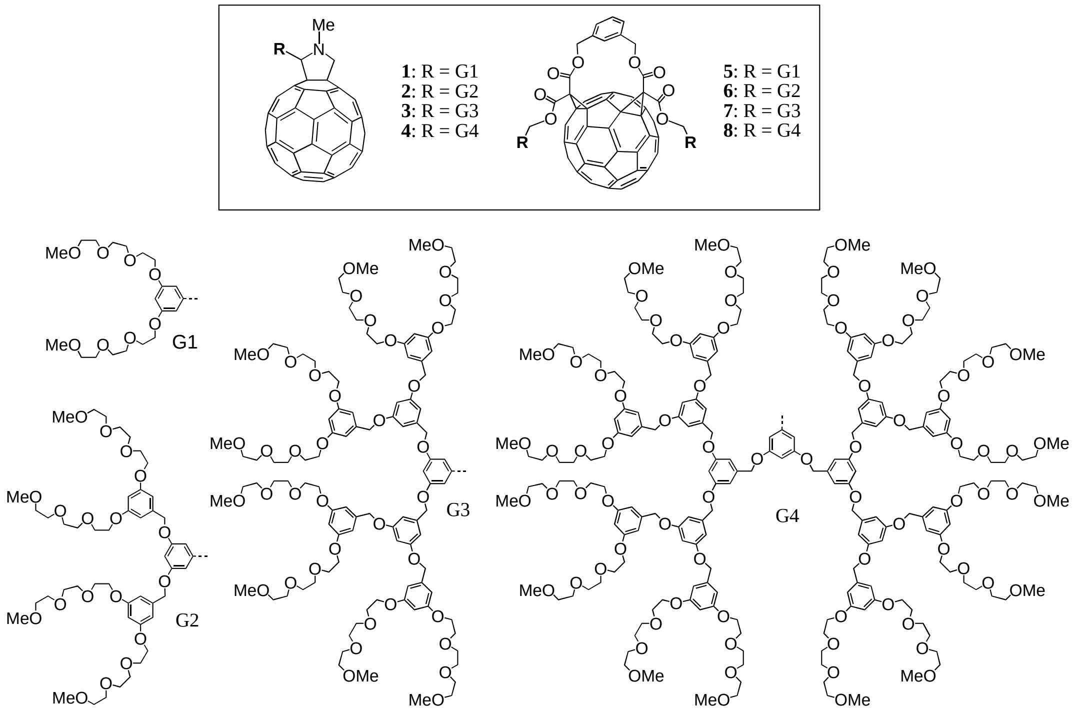


Figure 1. Fullerodendrimers **1**–**8**.

Table 1. Lifetime of the first triplet excited state of **1**–**8** in air equilibrated solutions determined by transient absorption at room temperature.

Compound	τ [ns] in PhMe	τ [ns] in CH_2Cl_2	τ [ns] in CH_3CN
1	279	598	–[a]
2	304	643	330
3	318	732	412
4	374	827	605
5	288	611	314
6	317	742	380
7	448	873	581
8	877	1103	1068

[a] Not soluble in this solvent.

For both series of dendrimers interesting trends can be obtained from the analysis of triplet lifetimes in air-equilibrated solutions (Table 1).[12] A steady increase of lifetimes is found by increasing the dendrimers size in all solvents, suggesting that the dendritic wedges are able to shield, at least partially, the fullerene core from external contacts with the solvent and from quenchers such as molecular oxygen. For compounds **1**–**4**, the increase is particularly marked in polar CH_3CN, where a better shielding of the fullerene chromophore is expected as a consequence of a tighter contact between the strongly nonpolar fullerene unit and the external dendritic wedges; 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 the 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 wedge is not able to provide a complete shielding of the central fulleropyrrolidine core in **4**.[12] The latter hypothesis was confirmed by computational studies. As shown in Figure 2, the calculated structure of **4** reveals that the dendritic shell is unable to completely cover the fullerene core (it must be noted that the calculations have been performed in the absence of solvent, our aim being only to estimate the possible degree of isolation). In contrast, the triplet lifetimes of **8**[15] in the three solvents lead towards a similar value; this suggests that the fullerene core is in a similar environment whatever the nature of the solvent is. In other words the C_{60} unit is, to a large extent, not surrounded by solvent molecules but substantially buried in the middle of the dendritic structure which is capable of creating a specific site-isolated microenvironment around the fullerene moiety. The latter hypothesis is quite reasonable based on the calculated structure of **8** (Figure 2) showing that the dendritic branches are able to fully cover the central fullerene core.

The dendritic effect evidenced for **1**–**8** might be useful to optimize the optical limiting properties characteristic of fullerene derivatives. Effectively, the intensity dependent absorption of fullerenes originates from larger absorption cross sections of excited states compared with that of the ground state,[18] therefore the increased triplet lifetime observed for the largest fullerodendrimers may allow for an effective limitation on a longer time scale. For practical applications, the use of solid devices is largely preferred to solutions and inclusion of fullerene derivatives in sol–gel glasses has shown interesting perspectives.[19] However, faster de-excitation dynamics and reduced triplet yields are typically observed for fullerene-doped sol–gel glasses when compared to solutions.[20] 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) inter-

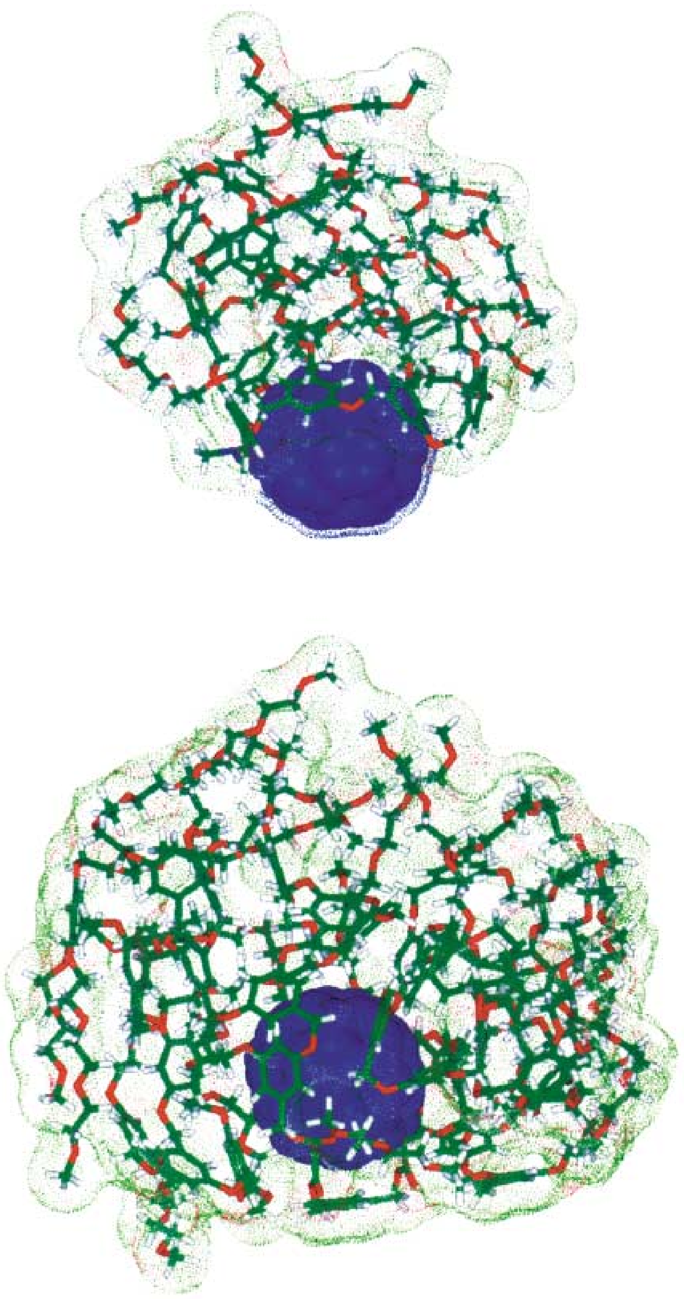


Figure 2. Calculated structure of fullerodendrimers **4** (top) and **8** (bottom).

actions between neighboring fullerene spheres due to aggregation.[20] Therefore, the encapsulation of the C_{60} core evidenced by the photophysical studies for both series of fullerodendrimers might also be useful to prevent such undesirable effects. The incorporation of fullerodendrimers **1**–**8** in sol–gel glasses has been easily achieved by soaking mesoporous silica glasses with a solution of **1**–**8**.[12] For the largest compounds, the resulting samples only contain well-dispersed fullerodendrimer molecules. Preliminary measurements on the resulting doped samples have revealed efficient optical limiting properties[12] and further studies are underway in order to determine the influence of the dendritic branches on the optical limiting behaviour of these composite materials.

Fullerodendrimers allow also an evaluation of the accessibility of the C_{60} core unit by studying bimolecular deactivation of its excited states by external quenchers. Recently Ito, Komatsu and co-workers have used this approach to investigate a series of fullerodendrimers (**9**–**11**) in which Fréchet-type dendrons have been connected to a fullerene moiety via an acetylene linker (Figure 3).[11] Both energy and electron transfer quenchers have been employed to show that the quenching rates of the fullerene triplet state are decreased as a function of the size of the dendrimer shell. These results further demonstrate that fullerene is an excellent functional group to probe the accessibility of a dendrimer core by external molecules.

Light Harvesting Dendrimers with a Fullerene Core

The fullerene C_{60} is also an attractive functional core for the preparation of light harvesting dendrimers. Effectively, its first singlet and triplet excited-states are relatively low in energy and photoinduced energy transfer events have been evidenced in some fullerene-based dyads.[21] In particular, photophysical investigations of some fulleropyrrolidine derivatives substituted with oligophenylenevinylene (OPV) moieties revealed a very efficient singlet–singlet OPV $\rightarrow C_{60}$ photoinduced energy transfer.[22] Based on this observation, dendrimers **12**–**14** with a fullerene core and peripheral OPV subunits (Figure 4) have been prepared.[23]

The photophysical properties of fullerodendrimers **12**–**14** have been investigated in CH_2Cl_2 solutions. Upon excitation at the OPV band maximum, dramatic quenching of OPV fluorescence is observed for all fullerodendrimers. This is attributed to an OPV $\rightarrow C_{60}$ singlet-singlet energy transfer process.[23] At 394 nm (corresponding to OPV band maxima) the molar absorptivities (ε) of these fullerodendrimers are 95800 for **12**, 134800 for **13** and 255100 $\text{M}^{-1}\,\text{cm}^{-1}$ for **14**. Since the ε of the ubiquitous *N*-methyl-fulleropyrrolidine at 394 nm

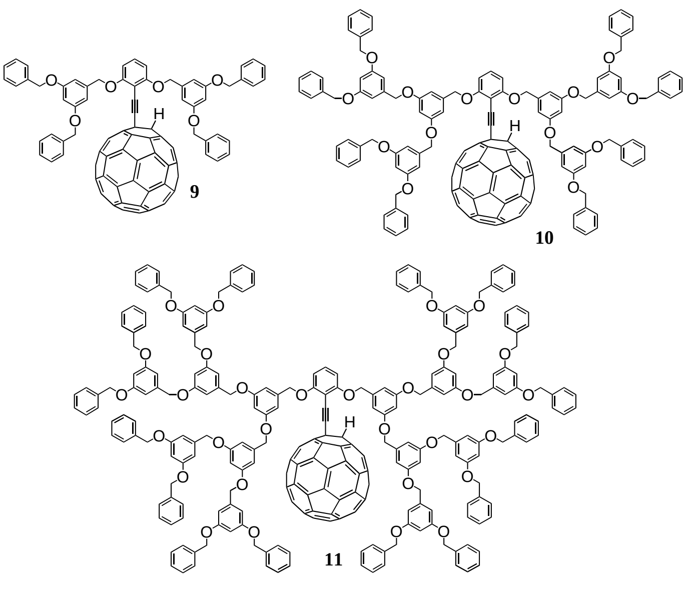
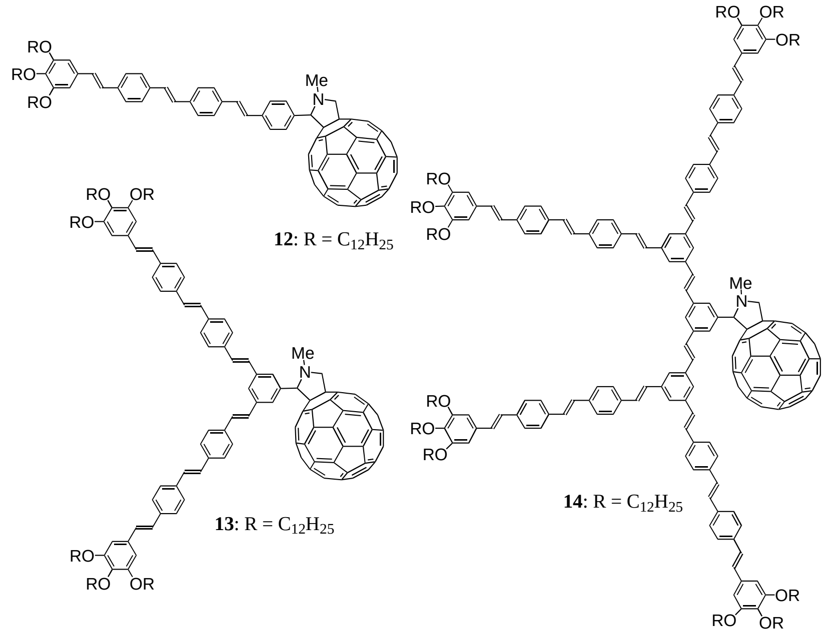


Figure 3. Fullerodendrimers **9**–**11**.

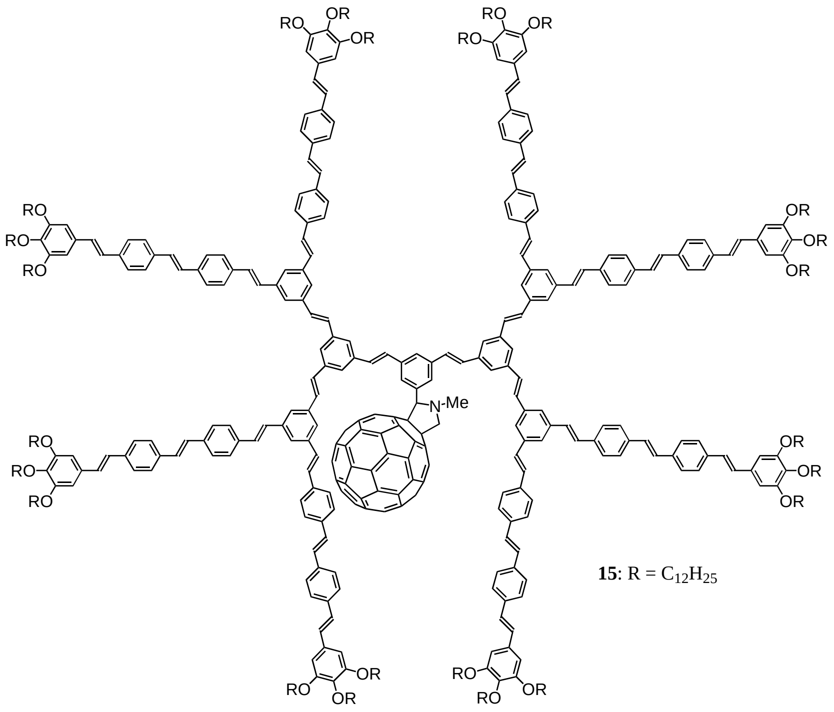


12: R = $C_{12}H_{25}$

13: R = $C_{12}H_{25}$

14: R = $C_{12}H_{25}$

Figure 4. Fullerodendrimers **12**–**14**.



15: R = $C_{12}H_{25}$

Figure 5. Fullerodendrimer **15**.

is only 7600 a remarkable light harvesting capability of the peripheral units relative to the central core is evidenced along the series.

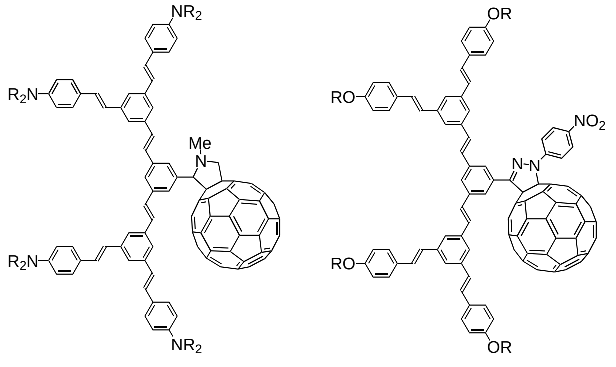
More recently, we have succeeded in the preparation of the next generation compound **15** (Figure 5) for which the molar absorptivity is about 450000 $\text{M}^{-1}\text{cm}^{-1}$.[24] The photophysical properties of **15** have not been yet investigated in detail; however, preliminary measurements in CH_2Cl_2 have revealed a strong quenching of the OPV fluorescence upon excitation at the OPV band maximum suggesting that the dendritic wedge is still capable of channeling the absorbed energy to the fullerene core.

Related compounds have been reported by Martin, Guldi, and co-workers.[25] The end-capping of the dendritic spacer with dibutylaniline units yielded the multicomponent photoactive system **16** in which the dendritic wedge plays at the same time the role of an antenna capable of channeling the absorbed energy to the fullerene core and of an electron donating unit (Figure 6). Photophysical investigations in benzonitrile solution have shown that, upon photoexcitation, efficient and fast energy transfer takes place from the initially excited antenna moiety to the fullerene core. This process populates the lowest fullerene singlet excited state which is able to promote electron transfer from the dendritic unit to the fullerene core. For **16**, relative to **12**–**14**, the charge separated state is significantly lower in energy than the fullerene singlet, as a result of the increased donating ability of the terminal dialkylaniline units. Therefore, the electron transfer is thermodynamically possible in **16** after the initial energy transfer event.

Langa and co-workers[26] have prepared fullerodendrimer **17** in which the phenylenevinylene dendritic wedge is connected to a pyrazolino[60]fullerene core rather than to a fulleropyrrolidine one as for **12**–**16** (Figure 6). Preliminary photophysical investigations suggest that the efficient energy transfer from the excited antenna moiety to the pyrazolino[60]fullerene core is followed by an electron transfer involving the fullerene moiety and the pyrazoline N atom.

Conclusion

Owing to their special photophysical properties, fullerene derivatives are good candidates for evidencing dendritic effects. In particular, we have shown that the triplet lifetimes



16: R = C_4H_9 **17**: R = $C_{12}H_{25}$

Figure 6. Fullerodendrimers **16** and **17**.

of a C_{60} core can be used to evaluate its degree of isolation from external contacts. In addition, the protective effect observed for fullerodendrimers **4** and **8** might be useful for optical limiting applications. On the other hand, the fullerene core can act as a terminal energy receptor in dendrimer-based light-harvesting systems. When the fullerodendrimer is further functionalized with a suitable electron donor, it may exhibit the essential features of an artificial photosynthetic system where an initial photoinduced energy transfer from the antenna to the C_{60} core can be followed by electron transfer.

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