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Functionalization of [60]fullerene with new light-collecting oligophenylenevinylene-terminated dendritic wedges

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Abstract—New oligophenylenevinylene-terminated phenylenevinylene dendrons have been prepared and attached to C_{60} by a 1,3-dipolar cycloaddition of the azomethine ylides generated in situ from the dendritic aldehydes and *N*-methylglycine. Preliminary photophysical investigations of the resulting fullerodendrimers have revealed interesting light-harvesting properties. © 2001 Published by Elsevier Science Ltd.

The synthesis and the study of dendrimer-based light-harvesting structures have attracted increased attention in the past decade.[1] In such systems, an array of peripheral chromophores is able to transfer the collected energy to the central core of the dendrimer thus mimicking the natural light-harvesting complex where antenna molecules collect sunlight and channel the absorbed energy to a single reaction center. The fullerene C_{60} is 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 fullerene-based dyads.[2–4] In particular, photophysical investigations of some fulleropyrrolidine derivatives substituted with oligophenylenevinylene (OPV) moieties revealed a very efficient singlet–singlet OPV→C_{60} photoinduced energy-transfer.[3,4] Based on this observation, dendrimers with a fullerene core and peripheral OPV subunits appear as potentially interesting systems with light-harvesting properties. In this paper, we report the synthesis of such fullerene derivatives and show that the C_{60} core in fullerodendrimers **1**–**3** is able to act as a terminal receptor of the excitation energy.

The preparation of compound **1** is depicted in Scheme 1. Compound **4** was obtained in two steps from *p*-bromobenzaldehyde as previously reported.[4] Reduction with $LiAlH_4$, bromination (CBr_4/PPh_3) and treatment with $P(OEt)_3$ afforded phosphonate **5** in an overall yield of 64%. Reaction of **5** with aldehyde **6**[5] under Wadsworth–Emmons conditions followed by treatment with CF_3CO_2H gave the OPV tetramer **7**. The functionalization of C_{60} was based on the 1,3-dipolar cycloaddition[6] of the azomethine ylide generated in situ from **7**. The reaction of C_{60} with **7** in the presence of an excess of *N*-methylglycine in refluxing toluene gave compound **1** in 46% yield. In addition, compound **8**, which was used as the reference compound for the absorption and emission properties, was prepared by $LiAlH_4$ reduction of **7**.

The preparation of bisphosphonate **10**, the key building block for the preparation of the OPV-terminated phenylenevinylene dendritic wedges,[7,8] is shown in Scheme 2. It was obtained in two steps from diol **9**.[9] Bromination using CBr_4/PPh_3 followed by treatment of the resulting bisbromide with $P(OEt)_3$ under Arbuzov conditions yielded **10** in an overall 66% yield. Reaction of **10** with aldehyde **6** in the presence of *t*-BuOK afforded compound **11** with 91% yield. Deprotection ($CF_3CO_2H/CH_2Cl_2/H_2O$) and subsequent treatment of the resulting aldehyde with C_{60} in the presence of *N*-methylglycine gave **2**. The next generation dendron was obtained in 90% yield by reaction of bisphosphonate **10** with the aldehyde resulting from the deprotection of **11**. Subsequent deprotection with CF_3CO_2H in CH_2Cl_2/H_2O yielded the corresponding aldehyde, which after reaction with C_{60} and *N*-methylglycine in refluxing toluene gave **3** in 25% yield. All the new compounds have been characterized by ^1H and ^{13}C NMR, and elemental analyses. In addition, the structures of fullerodendrimers **1**–**3** have also been confirmed by mass spectrometry.[10]

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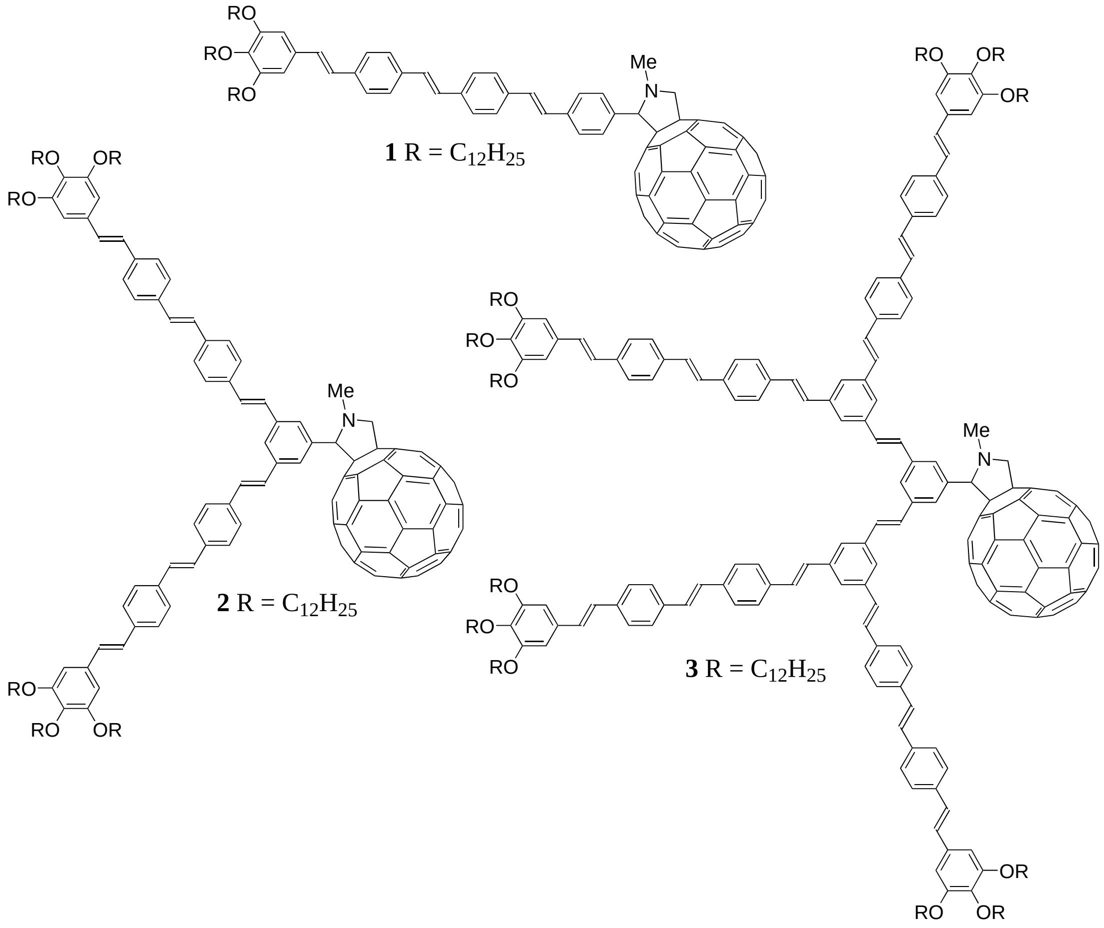
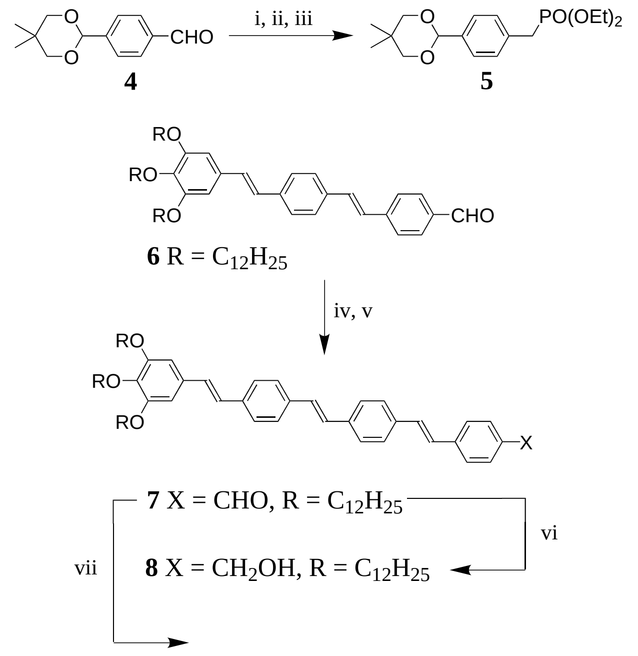


1 R = $C_{12}H_{25}$

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

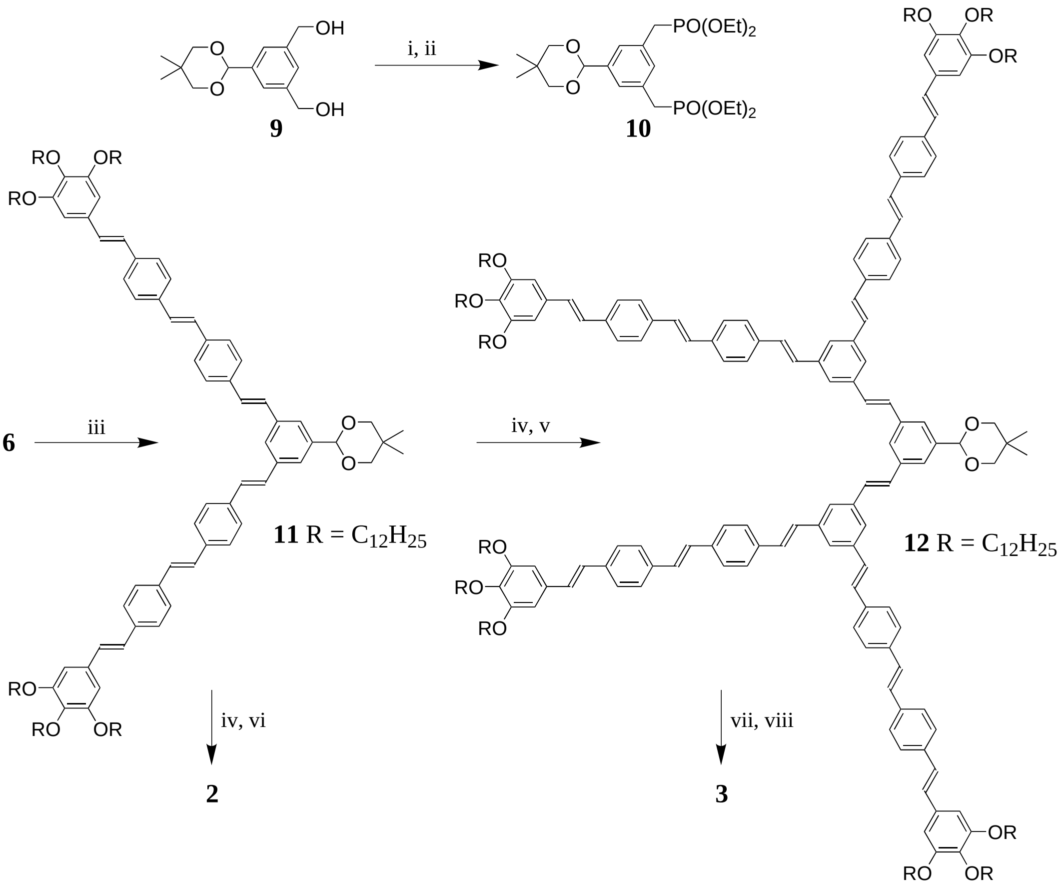
3 R = $C_{12}H_{25}$



Scheme 1. *Reagents and conditions*: (i) $LiAlH_4$, THF, 0°C (90%); (ii) PPh_3, CBr_4, THF, rt (84%); (iii) $P(OEt)_3$, 150°C (85%); (iv) **5**, *t*-BuOK, THF, 0°C to rt (88%); (v) CF_3CO_2H, CH_2Cl_2, H_2O, rt (96%); (vi) $LiAlH_4$, THF, 0°C (92%); (vii) C_{60}, *N*-methylglycine, toluene, Δ (46%).

The electronic absorption spectra of the model compounds **8**, **11**, and **12** in CH_2Cl_2 solutions are reported in Fig. 1. Interestingly, the λ_{max} is similar for the three compounds showing that the meta-substitution does not extend the conjugation in **11** and **12**. Indeed, compound **11** can be regarded as an assembly of two OPV tetramers sharing a phenyl ring. Similarly, the highest generation compound can be viewed as a combination of four OPV tetramers. The three molecules also exhibit intense fluorescence bands with λ_{max} at ca. 468 nm (Fig. 1). The fluorescence emission quantum yields (in the range 0.66–0.77) and excited lifetimes (1.1–1.3 ns) are similar along the series.

The absorption spectra of the fullerodendrimers **1**–**3** in CH_2Cl_2 are reported in Fig. 2 and present the spectral features of both component units. However, exact matching with the spectral profiles calculated by summing the absorption spectra of fulleropyrrolidine and the pertinent OPV fragment is never obtained, in line with previous reports.[4] This is particularly evident for **3** and might suggest substantial intramolecular ground state interaction between the fullerene core and the large aromatic network of **3**.[11] Upon excitation at the OPV band maximum, dramatic quenching of OPV fluorescence is observed for all fullerodendrimers. This is attributable to an OPV→C_{60} singlet–singlet energy transfer process,[3,4] as inferred by excitation spectra



Scheme 2. *Reagents and conditions*: (i) PPh_3, CBr_4, THF, rt (75%); (ii) $P(OEt)_3$, 150°C (88%); (iii) **10**, *t*-BuOK, THF, 0°C to rt (91%); (iv) CF_3CO_2H, CH_2Cl_2, H_2O, rt (90%); (v) **10**, *t*-BuOK, THF, 0°C to rt (85%); (vi) C_{60}, *N*-methylglycine, toluene, Δ (18%); (vii) CF_3CO_2H, CH_2Cl_2, H_2O, rt (90%); (viii) C_{60}, *N*-methylglycine, toluene, Δ (25%).

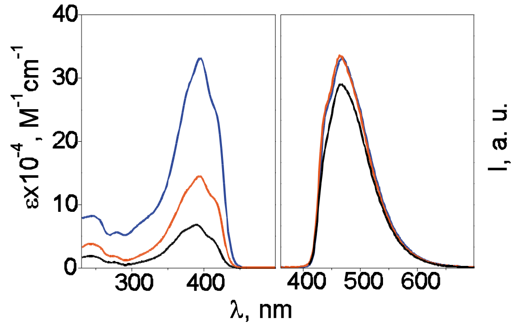


Figure 1. Absorption (left) and fluorescence (right, $\lambda_{exc}=314$ nm O.D. = 0.1) of compounds **8** (black), **11** (red) and **12** (blue). All the spectra have been recorded at 298 K in CH_2Cl_2 solutions.

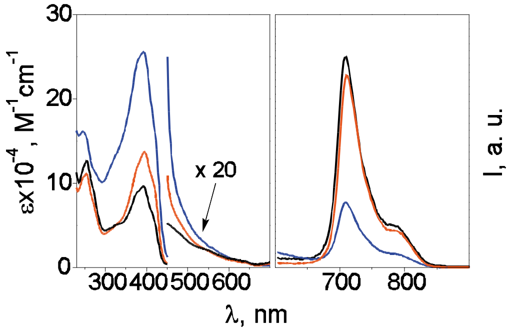


Figure 2. Absorption (left) and fluorescence (right, $\lambda_{exc}=500$ nm O.D. = 0.2) of **1** (black), **2** (red) and **3** (blue); the former are multiplied by a factor of 20 above 450 nm. All the spectra have been recorded at 298 K in CH_2Cl_2 solutions.

recorded at $\lambda_{em}=730$ nm. Simple comparison of the molar absorptivities at the excitation wavelength (394 nm, corresponding to OPV band maxima) allows quantification of the antenna effect obtained by increasing the generation number: 95,800 for **1**, 134,800 for **2** and 255,100 for **3**. When compared to fulleropyrrolidine for which the molar absorptivity is ca. 7600 at 394 nm, its functionalization with the OPV-terminated dendrons enables for the harvesting of increasing amounts of light.

Finally, it must also be pointed out that in CH_2Cl_2, selective excitation of the fullerene moiety at $\lambda>500$ nm does not evidence any fullerene fluorescence quenching for **1**. On the contrary, a progressive fluorescence yield decrease is observed for the larger OPV-C_{60} hybrids (Fig. 2). This suggests the occurrence of OPV→C_{60} photoinduced electron transfer,[12] to an increasing extent, along the series. Detailed photophysical investigations are currently in progress in order to elucidate the nature of all the photoinduced processes occurring in fullerodendrimers **1**–**3**.

In conclusion, an efficient synthetic methodology for preparation of OPV-terminated phenylenevinylene dendritic wedges has been developed. This enables us to prepare building blocks for the construction of new fullerodendrimers with light-harvesting properties. The further functionalization of these fullerodendrimers with a suitable electron donor is now underway to produce a multicomponent artificial photosynthetic system in which the photoinduced energy transfer to the C_{60} core is followed by electron transfer.

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10. Selected spectroscopic data for **1**: ^{1}H NMR (200 MHz, 25°C, $CDCl_3$): 7.79 (broad d, J=8.5 Hz, 2H), 7.59 (d, J=8.5 Hz, 2H), 7.50 (s, 8H), 7.13 (AB, J=16.5 Hz, 4H), 7.01 (AB, J=16.5 Hz, 2H), 6.72 (s, 2H), 5.01 (d, J=10 Hz, 1H), 4.95 (s, 1H), 4.28 (d, J=10 Hz, 1H), 4.03 (t, J=6.5 Hz, 4H), 3.98 (t, J=6.5 Hz, 2H), 2.83 (s, 3H), 1.83 (m, 6H), 1.50–1.20 (m, 54H), 0.89 (t, J=6.5 Hz, 9H); FAB-MS: 1712.6 (MH^+); anal. calcd for $C_{129}H_{101}NO_3$: C, 90.44; H, 5.94; N, 0.82; found C, 90.47; H, 6.13; N, 0.82. For **2**: ^{1}H NMR (400 MHz, 25°C, $CDCl_3$): 7.64 (s, 1H), 7.50 (m, 18H), 7.18 (s, 4H), 7.13 (s, 4H), 7.01 (AB, J=16.5 Hz, 4H), 6.73 (s, 4H), 5.05 (d, J=10 Hz, 1H), 4.99 (s, 1H), 4.32 (d, J=10 Hz, 1H), 4.04 (t, J=6.5 Hz, 8H), 3.98 (t, J=6.5 Hz, 4H), 2.89 (s, 3H), 1.83 (m, 12H), 1.50–1.20 (m, 108H), 0.89 (t, J=6.5 Hz, 18H); FAB-MS: 2572.5 (M^+); anal. calcd for $C_{189}H_{191}NO_6 \cdot H_2O$: C, 87.63; H, 7.51; N, 0.54; found C, 87.69; H, 7.59; N, 0.56. For **3**: ^{1}H NMR (400 MHz, 100°C, $C_2D_2Cl_4$): 8.02 (s, 2H), 7.77 (s, 1H), 7.50 (m, 38H), 7.34 (AB, J=16.5 Hz, 4H), 7.24 (AB, J=16.5 Hz, 8H), 7.18 (s, 8H), 7.03 (AB, J=16.5 Hz, 8H), 6.78 (s, 8H), 5.14 (d, J=10 Hz, 1H), 5.12 (s, 1H), 4.42 (d, J=10 Hz, 1H), 4.09 (t, J=6.5 Hz, 16H), 4.06 (t, J=6.5 Hz, 8H), 2.83 (s, 3H), 1.83 (m, 24H), 1.50–1.20 (m, 216H), 0.89 (t, J=6.5 Hz, 36H); MALDI-TOF-MS: 4498 (M^+); anal. calcd for $C_{325}H_{383}NO_{12} \cdot CHCl_3$: C, 84.84; H, 8.39; N, 0.30; found C, 85.09; H, 8.53; N, 0.29.
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