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Fullerene Derivatives Substituted with Differently Branched Phenyleneethynylene Dendrons: Synthesis, Electronic and Excited State Properties

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Fullerene derivatives functionalized with isomeric phenyleneethynylene-based dendrons possessing either 1,3,5-triethynylbenzene or 1,2,4-triethynylbenzene branching units have been prepared. The electrochemical properties of these compounds are not strongly dependent on the branching patterns since the corresponding redox processes are localized either on the C_{60} cage (acceptor unit) or on the dialkyloxybenzene moieties (donor units) at the dendron periphery. The photophysical investigations performed in CH_2Cl_2 have revealed an ultrafast dendron → C_{60} energy transfer in all these hybrid systems. Importantly, the different π-conjugation patterns in the two series have a dramatic effect on their electronic properties as attested by the differences observed in their absorption and emission spectra. The lower lying absorption onset and the wider spectral profile of the dyads with 1,2,4-triethynylbenzene branching units when compared to their 1,3,5-triethynylbenzene analogues clearly points out an improved light harvesting capability.

Introduction

The past several years have seen a growing interest in the synthesis and the study of dendrimers with a π-conjugated backbone.[1] Interestingly, their electronic properties can be easily tailored by either introducing various substituents,[2] changing the conjugation lengths of the different fragments within the dendritic shell,[3] or modulating the substitution pattern of the branching aromatic units.[4,5] The characteristic features of these compounds, such as large molar extinction coefficients and sometimes high fluorescence efficiencies, make them attractive photoactive components for the preparation of new sensors or photochemical molecular devices.[6] In particular, their absorption properties have been widely exploited for the design of light harvesting systems[7–9] in which the π-conjugated dendritic chromophore is able to transfer the collected light energy to the central core of the dendrimer.[10] Photophysical studies of such multicomponent molecular devices are not only important for the fundamental understanding of photoinduced processes, but appears of great interest for the design of new photovoltaic materials with optimized absorption properties,[11] or even organic light-emitting diodes.[12] Among the various terminal energy acceptors used in such light harvesting systems, [60]fullerene (C_{60}) has proven to be particularly interesting.[8,9] Effectively, its first singlet and triplet excited-states are relatively low in energy and photoinduced energy-transfer events have been evidenced in numerous fullerene-based dyads.[13] In this paper, we report the synthesis and the electronic properties of fullerene derivatives functionalized with isomeric phenyleneethynylene-based dendrons possessing 1,3,5-triethynylbenzene or 1,2,4-triethynylbenzene branching units (Figure 1). Whereas the π-conjugation of the dendritic antenna in **C_{60}-G1** and **C_{60}-G2** is rather limited due to the all-*meta*-branching scheme, the dendritic scaffold of **C_{60}-Y1** and **C_{60}-Y2** exhibits an increase of the conjugation length when going from the first to the second generation compound. The different conjugation length does not strongly affect the electrochemical processes since reduction is localized on the fullerene cage and oxi-

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dation on the dialkyloxybenzene peripheral units. On the other hand, the photophysical properties of the two families are significantly different. Indeed, the absorption of the antenna unit in **C_{60}-Y2** is significantly red-shifted when compared to the one in **C_{60}-G2**, thus the light harvesting capabilities of the system have been improved when going from **C_{60}-G2** to **C_{60}-Y2**.

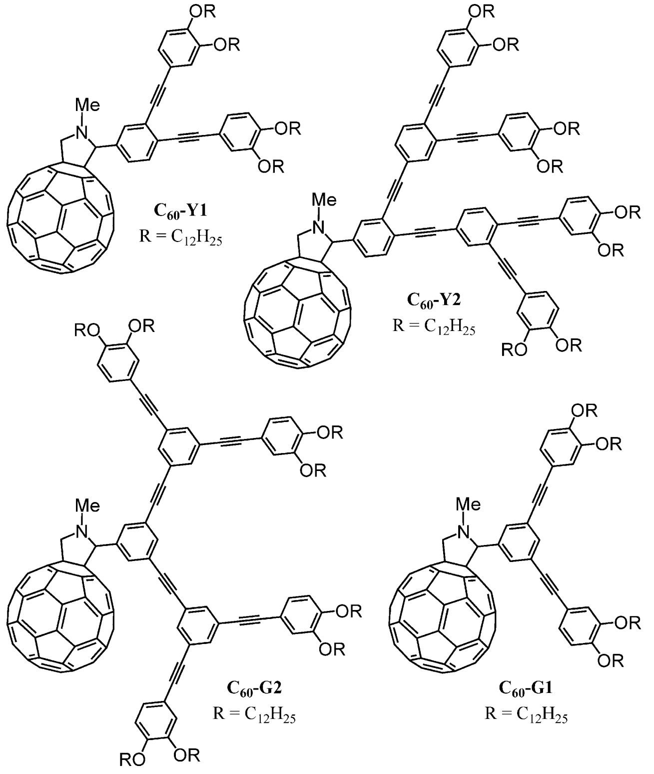
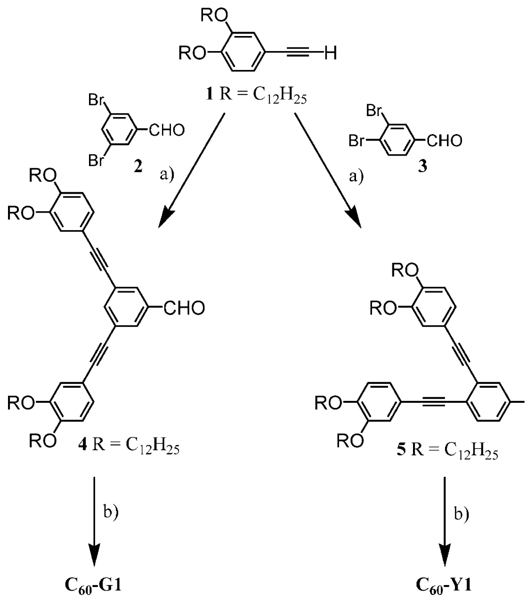


Figure 1. Compounds **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2**.

Results and Discussion

Synthesis

The preparation of the first generation derivatives **C_{60}-G1** and **C_{60}-Y1** is depicted in Scheme 1. Reaction of alkyne **1** with 3,5-dibromobenzaldehyde (**2**) and 3,4-dibromobenzaldehyde (**3**) under Sonogashira[14] conditions gave the first generation dendrons **4** and **5**, respectively. The functionalization of C_{60} was based on the 1,3-dipolar cycloaddition of the azomethine ylide[15] generated in situ from aldehydes **4** and **5**. The reaction of C_{60} with **4** in the presence of an excess of *N*-methylglycine in refluxing toluene gave compound **C_{60}-G1** in 61% yield. Compound **C_{60}-Y1** was obtained in 46% yield from **5**, C_{60} and *N*-methylglycine under similar conditions.



Scheme 1. Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 65 °C (**4**: 86%,**5**: 82%); (b) C_{60}, *N*-methylglycine, toluene, Δ (**C_{60}-G1**: 61%, **C_{60}-Y1**: 46%).

The ^1H NMR spectra of the pyrrolidinofullerene derivatives **C_{60}-G1** and **C_{60}-Y1** are in full agreement with the C_1 symmetry resulting from the presence of a stereogenic center in the pyrrolidine ring. At room temperature, the spectra exhibit the expected features with the characteristic signals arising from the 3,4-didodecyloxyphenyl units, a singlet for the methyl group, an AB quartet and a singlet for the pyrrolidine protons. For both **C_{60}-G1** and **C_{60}-Y1**, the signals corresponding to the protons of the phenyl group directly attached to the pyrrolidine ring are broad at room temperature. A variable-temperature NMR study showed clear coalescence, and the reversible narrowing of all these peaks reveals a dynamic effect. This indicates restricted rotation of the phenyl substituent on the pyrrolidine ring.[16] The ^1H NMR spectrum of compound **C_{60}-G1** recorded at 110 °C in $C_2D_2Cl_4$ is shown in Figure 2. At high temperatures, an AX_2 system is seen for the aromatic protons of the 3,5-diethynylphenyl unit. Indeed, the exchange between H_1 and $H_{1'}$ is fast on the NMR timescale under these conditions, and protons H_1 and $H_{1'}$ appear equivalent in the ^1H NMR spectrum. In contrast, by cooling the solution to –50 °C, this exchange resulting from the rotation of the phenyl unit around the phenyl-pyrrolidine bond becomes slow on the NMR timescale, as attested by the three sets of signals observed for the aromatic protons H_1, $H_{1'}$, and H_2. In contrast, the effect observed for **C_{60}-Y1** is resulting from a dynamic exchange between two atropisomers (**A** and **B**, Figure 2).[16] When the ^1H-NMR spectrum of **C_{60}-Y1** is recorded in $C_2D_2Cl_4$ at 100 °C (Figure 2), the dynamic exchange between the two atropisomers is fast on the NMR timescale, leading to a well resolved average spectrum under these conditions. By decreasing the temperature, a narrowing of all the peaks is also observed but the ^1H NMR spectrum becomes more complex. By –50 °C, the dynamic

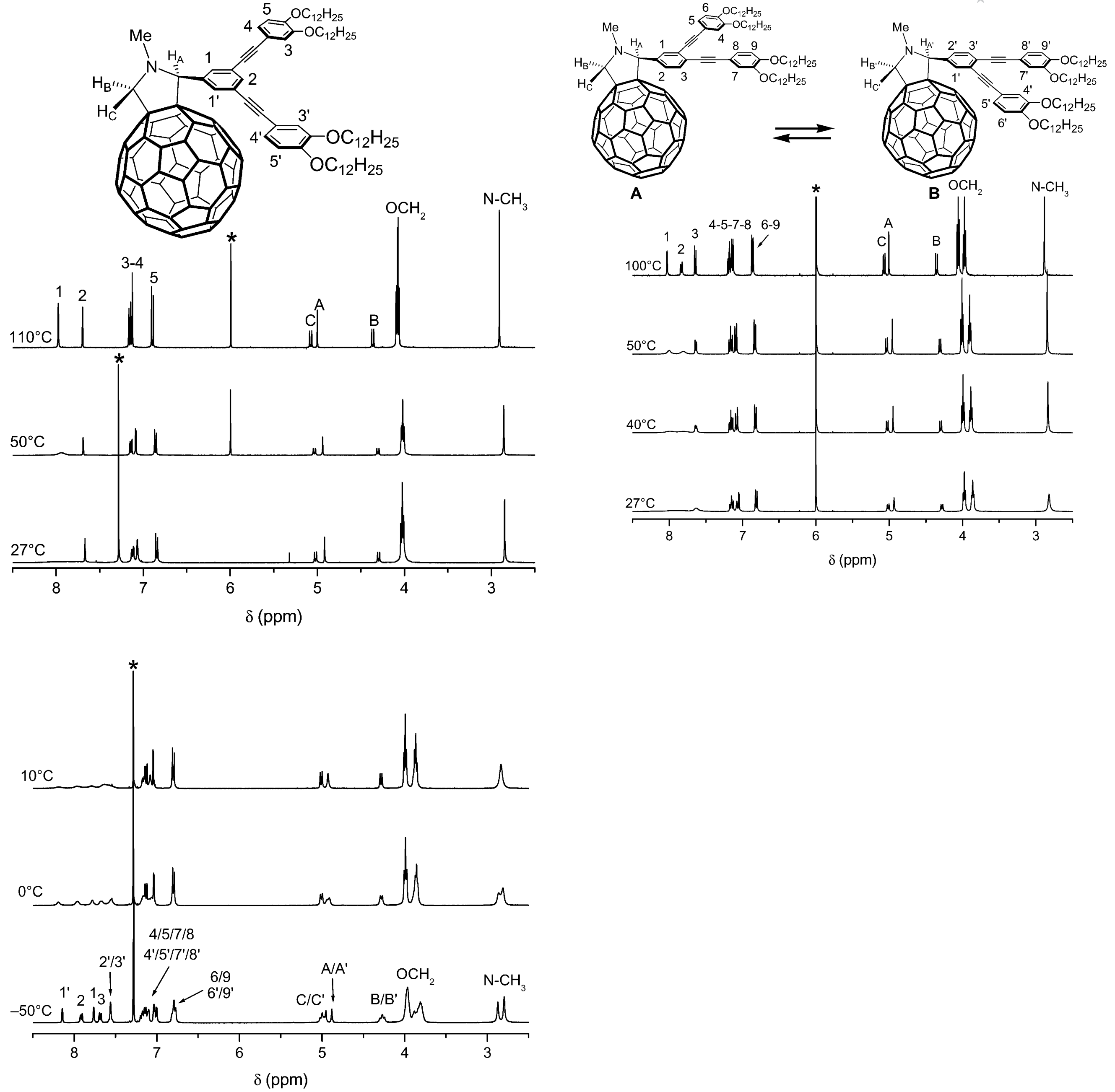
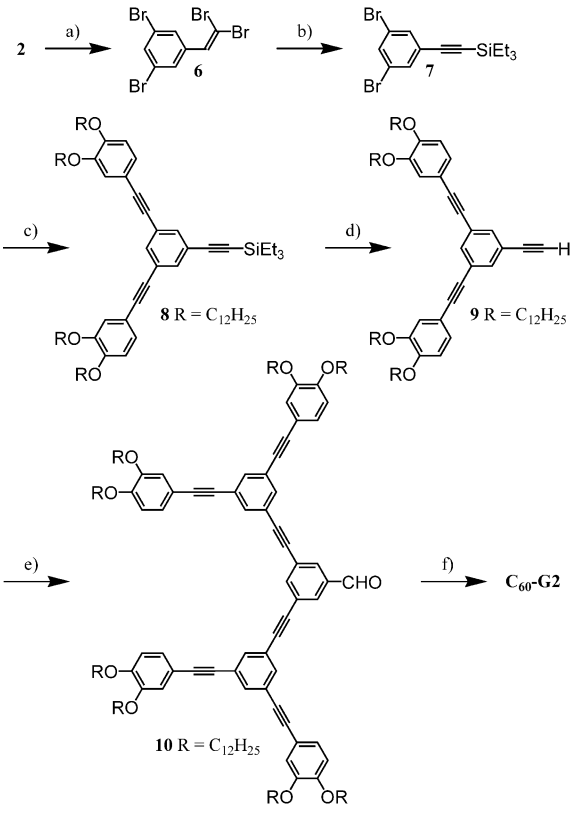


Figure 2. (top left) ^{1}H NMR spectra (400 MHz) of **C_{60}-G1** recorded in $C_2D_2Cl_4$ at 110 and 50 °C, and in $CDCl_3$ at room temperature (* solvent peak); (top right) ^{1}H NMR spectra (400 MHz) of **C_{60}-Y1** recorded in $C_2D_2Cl_4$ at 100, 50, 40 and 27 °C (* solvent peak); (bottom) ^{1}H NMR spectra (400 MHz) of **C_{60}-Y1** recorded in $CDCl_3$ at 10, 0, and –50 °C (* solvent peak; for the numbering, see Figure 2 top right).

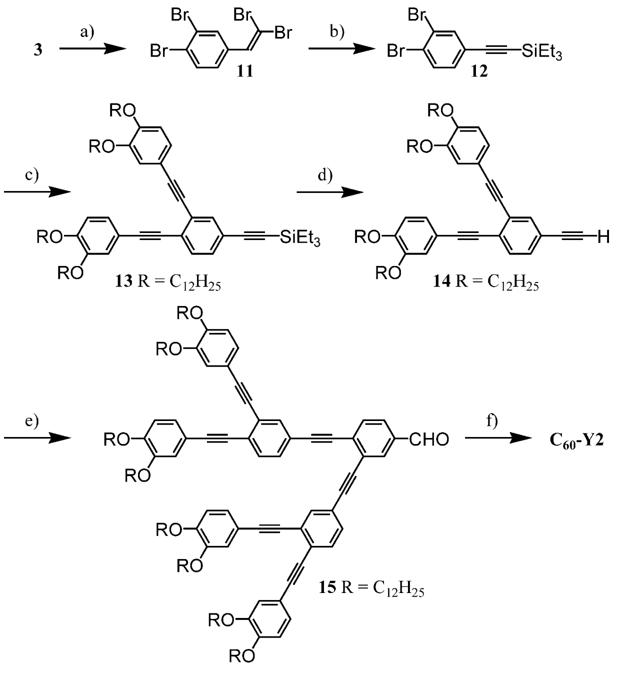
exchange between the two atropisomers is slow on the NMR timescale and the spectra of both conformers are clearly observed.

The synthesis of **C_{60}-G2** is depicted in Scheme 2. Treatment of **2** with $CBr_4/PPh_3/Zn$ under the conditions described by Corey–Fuchs[17] yielded dibromo olefin **6** in 95% yield. Elimination of HBr and halogen–metal exchange was best achieved with an excess of LDA in THF at –78 °C and the resulting anion was quenched with triethylsilyl chloride (TESCl) to give protected alkyne **7** in 70% yield. Compound **7** was subjected to a Pd-catalyzed cross-coupling reaction with **1** to yield dendron **8**. Subsequent treatment with K_2CO_3 in THF/MeOH gave terminal alkyne **9** in 91% yield. The second generation dendron **10** was then obtained in 96% yield by Pd-catalyzed cross-coupling between **9** and 3,5-dibromobenzaldehyde (**2**). Finally, reaction of **10** with C_{60} and *N*-methylglycine in refluxing toluene gave **C_{60}-G2** in 52% yield.

Compound **C_{60}-Y2** was prepared from 3,4-dibromobenzaldehyde (**3**) by following a similar synthetic route (Scheme 3). Dibromoolefination according to Corey–Fuchs provided **11** which after treatment with an excess of LDA



Scheme 2. Reagents and conditions: (a) CBr_4, PPh_3, Zn, CH_2Cl_2, 0 °C to room temp. (95%); (b) LDA, THF, –78 °C, then TESCl, THF, –78 °C (70%); (c) **1**, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 65 °C (99%); (d) K_2CO_3, THF, MeOH, room temp. (91%); (e) **2**, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 65 °C (96%); (f) C_{60}, *N*-methylglycine, toluene, Δ (52%).



Scheme 3. Reagents and conditions: (a) CBr_4, PPh_3, Zn, CH_2Cl_2, 0 °C to room temp. (95%); (b) LDA, THF, –78 °C, then TESCl, THF, –78 °C (63%); (c) **1**, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 65 °C (99%); (d) TBAF, THF, 0 °C (92%); (e) **3**, $Pd(PPh_3)_2Cl_2$, CuI, PPh_3, Et_3N, THF, 65 °C (84%); (f) C_{60}, *N*-methylglycine, toluene, Δ (50%).

in THF at –78 °C and quenching with TESCl afforded protected alkyne **12**. Compound **12** was subjected to a Pd-catalyzed cross-coupling reaction with **1** to yield the second generation dendron **13**. Treatment with tetra-*n*-butyl ammonium fluoride (TBAF) and subsequent reaction of the resulting **14** with **3** under Sonogashira conditions afforded dendron **15**. Treatment of **15** with C_{60} and *N*-methylglycine finally gave **C_{60}-Y2** in 50% yield.

Compounds **C_{60}-G2** and **C_{60}-Y2** are well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, or THF and complete spectroscopic characterization was easily achieved. Both ^{1}H and ^{13}C-NMR spectra are in full agreement with their C_1 symmetry resulting from the presence of a stereogenic center in the pyrrolidine ring. Variable-temperature ^{1}H NMR studies were also carried out with compounds **C_{60}-G2** and **C_{60}-Y2**. In both cases, a dynamic effect was evidenced and the results are closely similar to that discussed in detail for compounds **C_{60}-G1** and **C_{60}-Y1**. Finally, the structure of **C_{60}-G2** and **C_{60}-Y2** was confirmed by mass spectrometry. In both cases, the expected molecular ion peak was clearly observed.

In addition, compounds **G1**, **G2**, **Y1** and **Y2** (Figure 3) which were used as reference compounds, were prepared by diisobutylaluminum hydrid (DIBAL-H) reduction of benzaldehydes **4**, **10**, **5** and **15**, respectively.

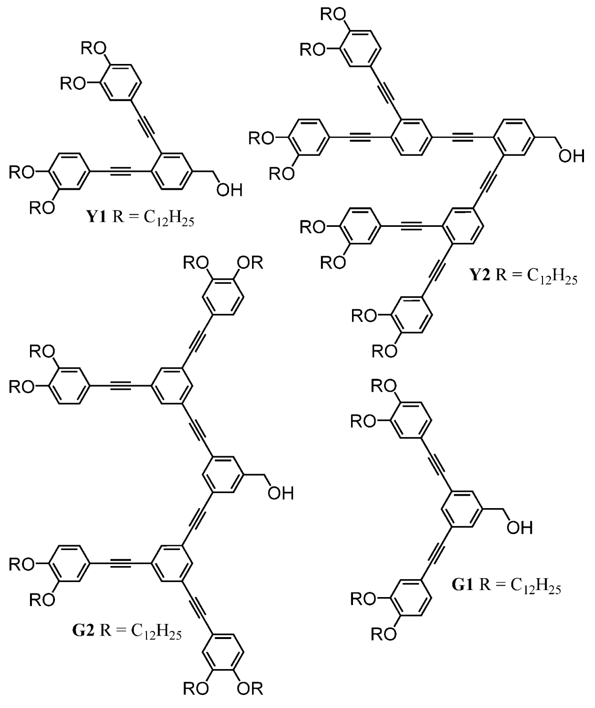


Figure 3. Model compounds **G1**, **G2**, **Y1**, and **Y2**.

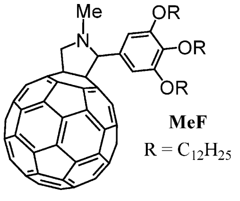
Electrochemistry

The cyclic voltammetric patterns of all the hybrid systems studied in CH_2Cl_2 show three reversible one-electron transfer processes in the cathodic region and two chemically irreversible electron-transfer processes corresponding to ill-defined peaks in the anodic region (Table 1). Comparison with the (*N*-methylpyrrolidino)fullerene reference compound **MeF** (Figure 4) allows us to assign the three observed reductions to the fullerene core. The C_{60}-based electron-transfer processes are almost unaffected by the presence of the phenyleneethynylene-based dendrons: only a very small positive shift of the half-wave potentials is observed.

Table 1. Half-wave potentials (in V vs. SCE) of **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, **C_{60}-Y2** and the corresponding reference compounds recorded in CH_2Cl_2 + 0.1 M nBu$_4$NPF$_6$ at room temperature using a glassy carbon working electrode.

	Red$_3$	*Red*$_2$	*Red*$_1$	*Ox*$_1$[a]	*Ox*$_2$[a]
MeF	–1.54	–1.01	–0.62		
C_{60}-Y1	–1.49	–0.97	–0.59	+1.41	+1.52
Y1				+1.35	
C_{60}-G1	–1.50	–0.97	–0.60	+1.40	+1.50
G1				+1.37	
C_{60}-Y2	–1.49	–0.97	–0.60	+1.41	+1.54
Y2				+1.41	
C_{60}-G2	–1.48	–0.96	–0.59	+1.40	+1.48
G2				+1.41	

[a] Chemically irreversible electron-transfer process; E_{pa} value at 0.2 V/s.



MeF

Figure 4. Model compound **MeF**.

In the cathodic region, the observed processes are assigned to the peripheral dialkyloxyphenyl units, as expected on the basis of the electrochemical properties of 1,2-dimethoxybenzene.[18] The oxidation process observed for the dendrons is very close to the first of the corresponding hybrid systems (E_{pa} values reported in Table 1), except for a slight negative shift in the case of **Y1** and **G1**. Moreover, the potential values corresponding to the first and second oxidation processes of all the C_{60}-based compounds are very similar without any significant difference between the **Y** and **G** series, thus suggesting that the electron transfers are mainly localized on the dialkyloxybenzene units. Surprisingly, in the case of **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2** two oxidation processes are observed, while for the corresponding dendrons only one process is present in the same potential window (Table 1). Although the evaluation of the number of electrons exchanged is precluded by the chemical irreversibility of the oxidation processes, these results suggest that the dialkyloxyphenyl units are no longer equivalent from the electrochemical point of view when the C_{60} unit is present.

Electronic Absorption Spectra

Reference compounds. The electronic absorption spectra of reference compounds **G1**, **G2**, **Y1** and **Y2** recorded in CH_2Cl_2 solutions at 298 K are shown in Figure 5. As expected, the increase in the size of the conjugated network for **G2** relative to **G1** results in a higher molar extinction coefficient. The absorption maxima as well as the end-absorptions are found similar for both **G1** and **G2**. This trend shows that the all-*meta* ramification does not promote efficient π-electronic conjugation within the branched dendritic structure, as already observed for related phenylenevinylene-based dendrimers.[5,8] In contrast, when going from **Y1** to **Y2**, an absorption onset at lower energy and a wider spectral profile are observed. This is due the presence of two π-conjugated moieties made of 3 *para*-phenylacetylene units in **Y2**. As a result, the larger delocalization in **Y2** leads to a 70 nm red-shift of the absorption onset relative to **Y1**. The absorption spectrum of **MeF** (Figure 6) shows the well-known features of pyrrolidinofullerenes.[19]

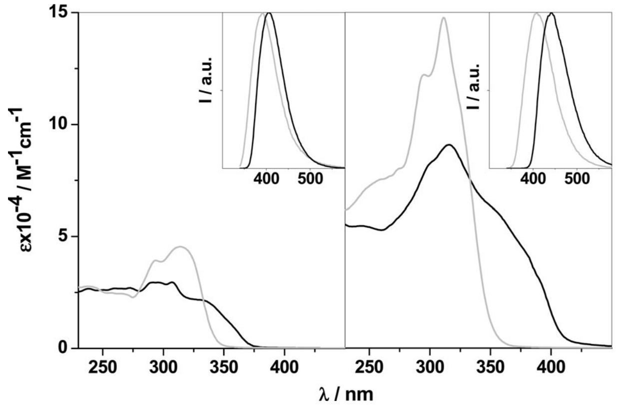


Figure 5. Absorption and normalized fluorescence spectra (inset) of **(a)** **Y1** (black), **G1** (grey); **(b)** **Y2** (black), **G2** (grey); CH_2Cl_2, 298 K. Emission spectra were recorded upon excitation at the absorption maximum (O.D. = 0.1).

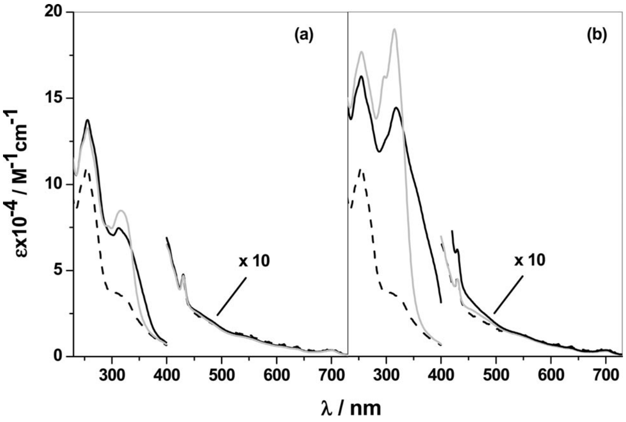


Figure 6. Absorption spectra of dyad compounds: **(a)** fulleropyrrolidine reference **MeF** (dashed), **C_{60}Y1** (black), **C_{60}G1** (grey); **(b)** fulleropyrrolidine reference **MeF** (dashed), **C_{60}Y2** (black), **C_{60}G2** (grey); CH_2Cl_2, 298 K. Beyond 400 nm, spectra are increased by a factor of 10 for display purposes.

Hybrid systems. The absorption spectra of the hybrid systems **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2** recorded in CH_2Cl_2 solutions are shown in Figure 6. In all cases the contributions from the fullerene and antenna components are clearly visible and distinguishable. Comparison of the absorption spectra of these hybrid systems with spectra resulting from the linear superimposition of the individual components (i.e. C_{60} and antenna) show no significant differences. This indicates that there are minimal ground state interactions between the fullerene and the conjugated dendritic subunits within these systems which would agree with the electrochemical data (vide supra).

Fully selective excitation of the dendritic unit in all hybrid systems is not possible due to overlap of their absorption profiles with that of the C_{60} unit. For **C_{60}-G1** and **C_{60}-Y1**, excitation at 310 nm corresponds to an average of 50% light absorption by the conjugated dendritic antenna. However, greater selectivity is possible for **C_{60}-G2** and **C_{60}-Y2** owing to the increased intensity of the absorption for the dendritic subunit of these compounds (selectivity as high as 86% is possible at 310 nm). Completely selective excitation of the C_{60} unit is possible for all hybrids at wavelengths > 460 nm.

Luminescence Properties and Photoinduced Processes

Reference compounds. **G1**, **G2**, **Y1** and **Y2** exhibit fluorescence bands in CH_2Cl_2 solution (Figure 5, Table 2). The singlet excited state lifetimes determined at room temperature are in the nanosecond range for all the compounds as typically observed for oligophenyleneethynylene systems.[20] The fluorescence spectra of **G1** and **G2** have practically the same shape, but the emission maximum of **G2** is slightly red-shifted (18 nm). The fluorescence quantum yield and the singlet excited state lifetime of **G1** are nearly identical to those of **G2**. When going from **Y1** to **Y2**, a larger red-shift of the emission maximum (40 nm) is observed. Furthermore, the emission quantum yields of **Y1** and **Y2** are much larger when compared to **G1** and **G2**. The latter observations point out the differences in π-delocalization in the two families of branched systems already deduced from their absorption features (see above).

Table 2. Luminescence properties in CH_2Cl_2 at 298 K.

	C_{60}			Dendron		
	λ_{max}[a] [nm]	Φ_{em}[b] ($\times 10^4$)	τ[c] [ns]	λ_{max}[a] [nm]	Φ_{em}[b]	τ[d] [ns]
MeF	714	5.50	1.19			
Y1				400	0.440	1.30
C_{60}-Y1	714	5.56	1.27	478	0.002	
G1				382	0.110	1.25
C_{60}-G1	712	4.74	1.22	438	0.001	
Y2				440	0.55	1.23
C_{60}-Y2	714	4.80	1.31	498	0.006	
G2				400	0.17	1.24
C_{60}-G2	714	5.69	1.32	422	0.002	

[a] Emission maxima from corrected spectra. [b] Emission quantum yields obtained in aerated samples. [c] Excited state lifetimes obtained in aerated samples; λ_{ex} = 337 nm. [d] Excited state lifetimes obtained in aerated samples; λ_{ex} = 465 nm.

Pyrrolidinofullerene **MeF** exhibit singlet excited state parameters (Table 2) identical to those of very similar systems reported previously.[19]

Hybrid systems. Following excitation at 310 nm, negligible fluorescence of the dendritic subunits is observed for **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2**. Indeed, when compared to the fluorescence intensity observed for reference compounds **G1**, **G2**, **Y1** and **Y2** under the same conditions, it appears that fluorescence is quenched by about two orders of magnitude (Table 2). Additionally, we observe a fluorescence band at approximately 710 mn which is almost identical in all cases to fluorescence observed for the fullerene reference compound **MeF**. Indeed the intensity of the bands observed for all hybrids is nearly equal to that of the fullerene reference **MeF** under the same experimental conditions (same absorbance at the excitation wavelength). These results suggest that efficient intramolecular singlet–singlet energy transfer takes place, as seen previously for analogous systems.[8] This process, clearly, must be on a timescale faster than that of the fluorescence of the conjugated dendritic units (≈ 1 ns). Excitation spectra taken in the range 300–450 nm at λ_{em} = 730 nm (fullerene fluorescence) show that sensitization of the C_{60} moiety occurs for **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2** giving strong support to a dendron→C_{60} singlet-singlet energy-transfer process. In previous studies involving similar hybrid systems, namely C_{60} derivatives bearing linear π-conjugated fragments, the initial energy-transfer event populates the lowest fullerene singlet excited state which is capable of promoting electron transfer from the oligomer to the C_{60} unit.[21] Actually, this can take place only when the charge separated state is lower in energy than the fullerene singlet. This is not the case here where the fulleropyrrolidine lowest singlet excited state is placed at 1.7 eV[8] above the ground state, i.e. substantially lower lying than the charge separated level which is located at about 2.9 eV for **C_{60}-G1**, **C_{60}-G2**, **C_{60}-Y1**, and **C_{60}-Y2**, as derived from the electrochemical data in CH_2Cl_2 (Table 1). Experimental evidence for a 100% efficient dendron→C_{60} energy transfer is also obtained in benzonitrile from fluorescence data. Thus, for the present dyads, the large difference in energy between the fullerene singlet and the charge separated state does not enable charge separation even in polar media, thus preventing tuning of photoinduced processes by solvent polarity as observed previously for a number of C_{60} multicomponent systems.[13]

Conclusions

Two series of isomeric dyads with differently branched phenyleneethynylene-based moieties and a pyrrolidinofullerene core have been prepared. The photophysical properties revealed an ultrafast and very efficient dendron→C_{60} energy transfer in all these hybrid systems. Importantly, the different π-conjugation patterns in **Y1–2** relative to **G1–2** have a dramatic effect on their electronic properties as attested by the differences observed in their absorption and emission spectra. The lower lying absorption onset and the wider spectral profile of **C_{60}-Y2** when compared to **C_{60}-G2** clearly points out an improved light harvesting capability for the former compound. On the other hand, the electrochemical properties of the two series of compounds are not strongly different since reduction and oxidation processes are mainly localized on the C_{60} core and the dialkoxybenzene peripheral units, respectively.

Experimental Section

General: Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled from sodium benzophenone ketyl. All reactions were performed in standard glassware under an inert Ar atmosphere. Evaporation and concentration were done at water aspirator pressure and drying in vacuo at 10^{-2} Torr. Column chromatography: silica gel 60 (230–400 mesh, 0.040–0.063 mm) was purchased from E. Merck. Thin-layer chromatography (TLC) was performed on glass sheets coated with silica gel 60 F_{254} purchased from E. Merck, visualization by UV light. IR spectra (cm^{-1}) were measured on an ATI Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 300 with solvent peaks as reference. FAB-mass spectra (*m*/*z*; % relative intensity) were taken on a *ZA HF* instrument with 4-nitrobenzyl alcohol as matrix. MALDI-TOF-mass spectra (*m*/*z*;% relative intensity) were carried out on a Bruker BIFLEX^{TM} matrix-assisted laser desorption time-of-flight mass spectrometer equipped with SCOUT^{TM} High Resolution Optics, an X-Y multi-sample probe and a gridless reflector. Ionization is accomplished with the 337 nm beam from a nitrogen laser with a repetition rate of 3 Hz. All data were acquired at a maximum accelerating potential of 20 kV in the linear positive ion mode. The output signal from the detector was digitized at a sampling rate of 1 GHz. A saturated solution of 1,8,9-trihydroxyanthracene (dithranol ALDRICH EC: 214-538-0) in CH_2Cl_2 was used as a matrix. Typically, a 1/1 mixture of the sample solution in CH_2Cl_2 was mixed with the matrix solution and 0.5 µL of the resulting mixture was deposited on the probe tip. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

General Procedure for the Preparation of Compounds 6 and 11: A mixture of CBr_4, PPh_3 and Zn dust in dry CH_2Cl_2 was stirred at room temperature for 24 h. The suspension was then cooled to 0 °C and the appropriate aldehyde dissolved in CH_2Cl_2 was added at once. The resulting mixture was slowly warmed to room temperature and stirred overnight. The resulting thick suspension was filtered and the solvents evaporated. The residue was dissolved in a minimum of CH_2Cl_2, then hexane was added to precipitate the remaining P-containing by-products. The resulting mixture was filtered and the solvents evaporated. The product was then purified as outlined in the following text.

Compound 6: This compound was prepared from **2** (3.00 g, 11.37 mmol), CBr_4 (18.85 g, 56.85 mmol), PPh_3 (14.91 g, 56.85 mmol) and Zn dust (3.72 g, 56.85 mmol) in CH_2Cl_2 (300 mL) and column chromatography (SiO_2, hexane) yielded **6** (4.55 g, 95%). Colorless solid. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.65 (t, *J* = 2 Hz, 1 H), 7.61 (2d, *J* = 2 Hz, 2 H), 7.37 (s, 1 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 138.3, 133.9, 133.8, 129.8, 122.8, 93.1 ppm.

Compound 11: This compound was prepared from **3** (1.00 g, 3.79 mmol), CBr_4 (6.28 g, 18.95 mmol), PPh_3 (4.97 g, 18.95 mmol) and Zn dust (1.24 g, 18.95 mmol) in CH_2Cl_2 (100 mL) and column chromatography (SiO_2, hexane) yielded **11** (1.51 g, 95%). Pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 2 Hz, 1 H), 7.62 (d, *J* = 8 Hz, 1 H), 7.38 (s, 1 H), 7.34 (dd, *J* = 8 and 2 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 135.8, 134.4, 133.5, 133.2, 128.2, 124.9, 124.8, 92.0 ppm.

General Procedure for the Preparation of Compounds 7 and 12: A solution of LDA in THF was slowly added to a solution of the appropriate dibromo olefine in THF at –78 °C under argon. After 2 h, a solution of triethylsilyl chloride was added at the same temperature. After 2 h a saturated aqueous NH_4Cl solution was added. The reaction mixture was diluted with hexane, washed with water, dried with $MgSO_4$ and the solvents evaporated. The product was then purified as outlined in the following text.

Compound 7: This compound was prepared from **6** (4.00 g, 9.53 mmol), LDA (38.12 mmol) and TESCl (10.48 mmol) in THF (250 mL) and column chromatography (SiO_2, hexane) yielded **7** (2.50 g, 70%). Colorless oil. IR (CH_2Cl_2): $\tilde{\nu}$ = 2164 (C≡C) cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ = 7.61 (t, *J* = 2 Hz, 1 H), 7.54 (d, *J* = 2 Hz, 2 H), 1.04 (m, 9 H), 0.68 (m, 6 H) ppm. ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 134.0, 133.4, 126.7, 122.5, 102.9, 95.2, 7.4, 4.3 ppm. $C_{14}H_{18}Br_2Si$ (374.19): calcd. C 44.94, H 4.85; found C 44.85, H 4.91.

Compound 12: This compound was prepared from **11** (1.59 g, 3.79 mmol), LDA (15.16 mmol) and TESCl (4.17 mmol) in THF (100 mL) and column chromatography (SiO_2, hexane) yielded **10** (0.89 g, 63%). Colorless solid (m.p. 155 °C). IR (KBr): $\tilde{\nu}$ = 2162 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.72 (d, *J* = 2 Hz, 1 H), 7.55 (d, *J* = 8 Hz, 1 H), 7.25 (dd, *J* = 8 and 2 Hz, 1 H), 1.05 (m, 9 H), 0.7 (m, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 136.7, 133.3, 131.7, 125.0, 124.5, 124.0, 103.5, 94.6, 7.5, 4.3 ppm. $C_{14}H_{18}Br_2Si$ (374.19): calcd. C 44.94, H 4.85; found C 44.99, H 4.84.

Compound 9: K_2CO_3 (50 mg, 0.36 mmol) was added to a solution of **8** (1.55 g, 1.99 mmol) in a mixture of THF (10 mL) and MeOH (100 mL). After 3 h, the reaction mixture was filtered through a celite pad and the solvent evaporated. The crude product was diluted with dichloromethane. The resulting solution was washed with water, dried with $MgSO_4$ and the solvents evaporated. Column chromatography (SiO_2, hexane) yielded **9** (1.20 g, 91%). Pale yellow glassy product. IR (KBr): $\tilde{\nu}$ = 3304 (C≡C–H), 2152 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (t, *J* = 2 Hz, 1 H), 7.60 (d, *J* = 2 Hz, 2 H), 5.30 (s, 8 H), 3.12 (s, 1 H), 1.14 (s, 42 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 134.7, 134.6, 132.4, 132.3, 132.0, 131.5, 131.1, 123.9, 123.8, 123.0, 122.5, 106.5, 93.1, 90.4, 89.3, 81.9, 78.5, 18.7, 11.3 ppm. $C_{46}H_{54}Si_2\cdot H_2O$ (681.11): calcd. C 81.13, H 8.30; found C 81.15, H 8.28.

Compound 14: A 1 M solution of TBAF in THF (2.60 mL, 2.60 mmol) was added to a solution of **13** (3.00 g, 2.60 mmol) in THF (150 mL) at 0 °C under argon. After 2 h, water was added. The reaction mixture was diluted with dichloromethane, washed with water, dried with $MgSO_4$ and the solvent was evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **14** (2.45 g, 92%). Pale yellow glassy product. IR (KBr): $\tilde{\nu}$ = 3290 (C≡C–H), 2155 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.66 (d, *J* = 2 Hz, 1 H), 7.47 (d, *J* = 8 Hz, 1 H), 7.36 (dd, *J* = 2 and 8 Hz, 1 H), 7.13 (2 dd, *J* = 2 and 8 Hz, 2 H), 7.05 (d, *J* = 2 Hz, 2 H), 6.81 (d, *J* = 8 Hz, 2 H), 4.00 (2t, *J* = 7 Hz, 4 H), 3.89 (2t, *J* = 7 Hz, 4 H), 3.17 (s, 1 H), 1.81 (m, 8 H), 1.27–1.76 (m, 72 H), 0.89 (t, *J* = 7 Hz, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.0, 149.9, 148.8, 134.8, 131.2, 131.0, 126.4, 126.3, 125.0, 124.9, 121.4, 116.5, 115.1, 113.0, 96.0, 94.6, 86.6, 86.0, 82.6, 79.0, 69.0, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 26.0, 22.7, 14.1 ppm. $C_{72}H_{110}O_4$ (1039.64): calcd. C 83.18, H 10.66; found C 83.37, H 10.69.

General Procedure for the Preparation of Compounds 4, 5, 8, 10, 13 and 15: To an oven-dried glass screw capped tube were added all solids including the halide, alkyne, CuI, PPh_3 and palladium catalyst. The atmosphere was removed via vacuum and replaced with dry argon (3×). THF and triethylamine were added by syringe and the reaction was heated at 65 °C in an oil bath while stirring. Upon cooling the reaction mixture was filtered via gravity filtration to remove solids and diluted with dichloromethane. The reaction mixture was extracted with an aqueous NH_4Cl solution. The organic layer was dried with $MgSO_4$ and the solvent was evaporated. The product was then purified as outlined in the following text.

Compound 4: This compound was prepared from **2** (0.40 g, 1.52 mmol), **1** (2.14 g, 4.55 mmol), $Pd(PPh_3)_2Cl_2$ (128 mg, 0.18 mmol), CuI (14.5 mg, 0.08 mmol) and PPh_3 (60 mg, 0.23 mmol) in THF/Et_3N, 4:1 (10 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 9:1) yielded **4** (1.36 g, 86%). Yellow glassy product. IR (KBr): $\tilde{\nu}$ = 2151 (C≡C), 1704 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1 H), 7.93 (d, *J* = 2 Hz, 2 H), 7.88 (t, *J* = 2 Hz, 1 H), 7.12 (dd, *J* = 8 and 2 Hz, 2 H), 7.05 (d, *J* = 2 Hz, 2 H), 6.86 (d, *J* = 8 Hz, 2 H), 4.03 (2 t, *J* = 7 Hz, 8 H), 1.83 (m, 8 H), 1.28–1.49 (m, 72 H), 0.89 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 191.0, 150.2, 149.8, 139.2, 136.6, 131.4, 125.2, 116.7, 114.4, 113.2, 91.9, 85.8, 69.3, 69.2, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 26.0, 22.7, 14.1 ppm. $C_{71}H_{110}O_5$ (1043.63): calcd. C 81.71, H 10.62; found C 81.55, H 10.76.

Compound 5: This compound was prepared from **1** (2.01 g, 4.26 mmol), **3** (0.38 g, 1.42 mmol), $Pd(PPh_3)_2Cl_2$ (120.00 mg, 0.17 mmol), CuI (13.5 mg, 0.07 mmol) and PPh_3 (56 mg, 0.21 mmol) in THF/Et_3N, 4:1 (10 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 4:1) yielded **C** (1.21 g, 82%). Glassy product. IR (KBr): $\tilde{\nu}$ = 2151 (C≡C), 1702 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.00 (s, 1 H), 8.02 (d, *J* = 2 Hz, 1 H), 7.79 (dd, *J* = 8 and 2 Hz, 1 H), 7.67 (d, *J* = 8 Hz, 1 H), 7.17 (2 dd, *J* = 8 and 2 Hz, 2 H), 7.07 (2 d, *J* = 2 Hz, 2 H), 6.83 (2 d, *J* = 8 Hz, 2 H), 4.01 (2 t, *J* = 7 Hz, 4 H), 3.90 (2 t, *J* = 7 Hz, 4 H), 1.83 (m, 8 H), 1.27–1.56 (m, 72 H), 0.89 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 190.8, 150.4, 150.1, 148.8, 134.9, 132.9, 131.8, 131.7, 127.7, 126.9, 125.3, 125.0, 116.6, 116.5, 114.8, 114.6, 113.1, 113.0, 98.3, 95.4, 86.7, 85.8, 69.1, 31.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 26.0, 22.7, 14.1 ppm. $C_{71}H_{110}O_5\cdot 0.5H_2O$ (1052.64): calcd. C 81.01, H 10.63; found C 81.06, H 10.64.

Compound 8: This compound was prepared from **7** (500 mg, 1.34 mmol), **1** (1.89 g, 4.01 mmol), $Pd(PPh_3)_2Cl_2$ (113 mg, 0.16 mmol), CuI (13 mg, 0.07 mmol) and PPh_3 (53 mg, 0.20 mmol) in THF/Et_3N, 4:1 (10 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 8:2) yielded **8** (1.54 g, 99%). Glassy product. IR (KBr): $\tilde{\nu}$ = 2151 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.59 (t, *J* = 2 Hz, 1 H), 7.55 (d, *J* = 2 Hz, 2 H), 7.09 (2 dd, *J* = 8 and 2 Hz, 2 H), 7.03 (d, *J* = 2 Hz, 2 H), 6.84 (d, *J* = 8 Hz, 2 H), 4.02 (t, *J* = 7 Hz, 8 H), 1.84 (m, 8 H), 1.27–1.56 (m, 72 H), 1.06 (t, *J* = 8 Hz, 9 H), 0.89 (t, *J* = 7 Hz, 12 H), 0.69 (q, *J* = 8 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.0, 148.8, 134.0, 133.9, 125.1, 124.2, 124.0, 116.7, 114.9, 113.3, 104.8, 92.9, 90.8, 86.3, 69.3, 69.2, 53.4, 31.9, 29.8, 29.7, 29.6, 29.4, 29.3, 29.2, 29.1, 26.1, 26.0, 22.7, 14.1, 7.5, 4.4 ppm. $C_{78}H_{124}O_4Si$ (1153.90): calcd. C 81.19, H 10.83; found C 81.15, H 10.80.

Compound 10: This compound was prepared from **2** (169 mg, 0.64 mmol), **9** (2.00 g, 1.92 mmol), $Pd(PPh_3)_2Cl_2$ (54 mg, 0.08 mmol), CuI (6 mg, 0.03 mmol) and PPh_3 (25 mg, 0.10 mmol) in THF/Et_3N, 4:1 (5 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **10** (1.34 g, 96%). Glassy product. IR (KBr): $\tilde{\nu}$ = 2150 (C≡C), 1702 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 8.00 (d, *J* = 2 Hz, 2 H), 7.91 (t, *J* = 2 Hz, 1 H), 7.66 (t, *J* = 2 Hz, 2 H), 7.63 (d, *J* = 2 Hz, 4 H), 7.12 (dd, *J* = 2 and 8 Hz, 4 H), 7.05 (d, *J* = 2 Hz, 4 H), 6.85 (d, *J* = 8 Hz, 4 H), 4.03 (t, *J* = 7 Hz, 16 H), 1.83 (m, 16 H), 1.28–1.57 (m, 144 H), 0.91 (m, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.1, 148.8, 139.5, 136.7, 134.4, 133.6, 132.3, 125.1, 124.6, 124.5, 123.0, 116.7, 114.7, 113.2, 91.2, 90.2, 87.9, 86.2, 69.3, 69.1, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 26.1, 26.0, 22.7, 14.1 ppm. $C_{151}H_{222}O_9$ (2181.41): calcd. C 83.14, H 10.26; found C 83.24, H 10.27.

Compound 13: This compound was prepared from **1** (1.13 g, 2.40 mmol), **12** (0.30 g, 0.80 mmol), $Pd(PPh_3)_2Cl_2$ (68 mg, 0.10 mmol), CuI (7.5 mg, 0.04 mmol) and PPh_3 (32 mg, 0.12 mmol) in THF/Et_3N, 4:1 (10 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 9:1) yielded **13** (0.92 g, 99%). Glassy product. IR (KBr): $\tilde{\nu}$ = 2154 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 2 Hz, 1 H), 7.45 (d, *J* = 8 Hz, 1 H), 7.36 (dd, *J* = 8 and 2 Hz, 1 H), 7.13 (2 dd, *J* = 8 and 2 Hz, 2 H), 7.05 (d, *J* = 2 Hz, 2 H), 6.80 (d, *J* = 8 Hz, 2 H), 3.97 (2t, *J* = 7 Hz, 4 H), 3.88 (2t, *J* = 7 Hz, 4 H), 1.80 (m, 8 H), 1.19–1.56 (m, 72 H), 1.06 (t, *J* = 8 Hz, 9 H), 0.89 (t, *J* = 7 Hz, 12 H), 0.69 (q, *J* = 8 Hz, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.4, 150.0, 149.9, 148.7, 148.6, 134.7, 131.0, 130.8, 126.2, 126.0, 125.9, 124.9, 122.6, 117.0, 116.5, 115.2, 113.9, 113.0, 105.3, 95.8, 94.4, 93.8, 86.8, 86.1, 69.1, 69.0, 32.0, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 26.1, 26.0, 25.9, 22.7, 14.0, 7.4, 4.3 ppm. $C_{78}H_{124}O_4Si$ (1153.90): calcd. C 81.19, H 10.83; found C 81.14, H 10.88.

Compound 15: This compound was prepared from **3** (169 mg, 0.64 mmol), **14** (2.00 g, 1.92 mmol), $Pd(PPh_3)_2Cl_2$ (54 mg, 0.08 mmol), CuI (6 mg, 0.03 mmol) and PPh_3 (25 mg, 0.10 mmol) in THF/Et_3N, 4:1 (7 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **15** (1.17 g, 84%). Glassy product. IR (KBr): $\tilde{\nu}$ = 2150 (C≡C), 1702 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 10.04 (s, 1 H), 8.07 (broad s, 1 H), 7.85 (broad d, *J* = 8 Hz, 1 H), 7.79 (m, 2 H), 7.72 (d, *J* = 8 Hz, 1 H), 7.52 (m, 4 H), 7.14 (m, 4 H), 7.05 (m, 2 H), 7.02 (m, 2 H), 6.77 (2d, *J* = 8 Hz, 4 H), 4.00 (t, *J* = 7 Hz, 4 H), 3.87 (m, 12 H), 1.81 (m, 16 H), 1.27–1.56 (m, 144 H), 0.89 (t, *J* = 7 Hz, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.2, 150.1, 150.0, 149.9, 148.8, 148.7, 135.4, 134.6, 134.5, 133.1, 132.3, 131.5, 131.2, 130.6, 130.5, 129.3, 126.7, 126.4, 125.2, 125.1, 122.0, 121.8, 116.6, 116.5, 115.1, 115.0, 114.9, 114.8, 113.1, 96.9, 96.5, 96.3, 95.0, 94.9, 94.4, 86.6, 89.0, 86.9, 86.0, 85.9, 69.1, 69.0, 68.9, 32.0, 29.7, 29.5, 29.4, 29.3, 29.2, 26.1, 26.0, 23.0, 14.1 ppm. $C_{151}H_{222}O_9$ (2181.37): calcd. C 83.14, H 10.26; found C 83.17, H 10.28.

General Procedure for the Preparation of G1, G2, Y1, and Y2: A 1 M DIBAL-H solution in hexane was slowly added to a solution of the appropriate benzaldehyde in THF at 0 °C under argon. After 3 h, methanol then water were added. The reaction mixture was filtered through a celite pad, dried with $MgSO_4$ and the solvent was evaporated. The product was then purified as outlined in the following text.

Compound G1: This compound was prepared from **4** (200 mg, 0.19 mmol), DIBAL-H (0.50 mL), in THF (7 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **G1** (158.00 mg, 79%). Yellow glassy product. IR (KBr): $\tilde{\nu}$ = 3212 (–OH), 2151 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60 (t, *J* = 2 Hz, 1 H), 7.44 (d, *J* = 2 Hz, 2 H), 7.10 (dd, *J* = 8 and 2 Hz, 2 H), 7.04 (d, *J* = 2 Hz, 2 H), 6.83 (d, *J* = 8 Hz, 2 H), 4.68 (s, 2 H), 4.01 (t, *J* = 7 Hz, 8 H), 1.84 (m, 8 H), 1.28–1.49 (m, 72 H), 0.90 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.7, 148.6, 141.4, 133.2, 129.0, 125.0, 124.0, 116.6, 115.0, 113.1, 90.3, 86.9, 69.2, 69.1, 64.4, 31.9, 29.7, 29.65, 29.6, 29.4, 29.35, 29.2, 29.15, 25.9, 22.7, 14.0 ppm. $C_{71}H_{112}O_5$ (1045.65): calcd. C 81.54, H 10.80; found C 81.03, H 10.83.

Compound G2: This compound was prepared from **10** (200 mg, 0.09 mmol), DIBAL-H (0.23 mL), in THF (14 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **G2** (160 mg, 80%). Yellow glassy product. IR (KBr): $\tilde{\nu}$ = 3200 (–OH), 2152 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.64 (m, 6 H), 7.51 (s, 3 H), 7.12 (dd, J = 2 and 8 Hz, 4 H), 7.05 (d, J = 2 Hz, 4 H), 6.84 (d, J = 8 Hz, 4 H), 4.72 (s, 2 H), 4.03 (t, J = 7 Hz, 16 H), 1.83 (m, 16 H), 1.29–1.49 (m, 144 H), 0.89 (m, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 148.7, 141.7, 133.9, 133.6, 133.5, 129.9, 125.1, 124.4, 123.5, 123.4, 116.7, 114.8, 113.2, 90.9, 89.2, 88.7, 86.3, 69.3, 69.2, 64.3, 31.9, 29.7, 29.65, 29.6, 29.4, 29.35, 29.2, 29.15, 26.0, 22.7, 22.4, 14.1 ppm. $C_{151}H_{224}O_9$ (2183.39): calcd. C 83.05, H 10.35; found C 83.03, H 10.54.

Compound Y1: This compound was prepared from **5** (200 mg, 0.19 mmol), DIBAL-H (0.50 mL), in THF (7 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **Y1** (163.00 mg, 81%). Yellow glassy product. IR (KBr): $\tilde{\nu}$ = 3678 (–OH), 2220 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53 (m, 2 H), 7.27 (s, 1 H), 7.14 (2dd, J = 8 and 2 Hz, 2 H), 7.06 (2d, J = 2 Hz, 2 H), 6.81 (d, J = 8 Hz, 2 H), 4.71 (d, J = 5 Hz, 2 H), 4.00 (2t, J = 7 Hz, 4 H), 3.89 (2t, J = 7 Hz, 4 H), 1.80 (m, 8 H), 1.27–1.58 (m, 72 H), 0.89 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.8, 149.75, 148.7, 140.5, 131.5, 129.5, 126.2, 126.0, 125.1, 124.9, 116.6, 115.4, 115.3, 113.1, 94.0, 93.9, 86.8, 86.8, 69.15, 69.1, 64.6, 31.9, 29.7, 29.65, 29.6, 29.5, 29.4, 29.35, 29.2, 26.1, 26.0, 22.7, 14.1 ppm. $C_{71}H_{112}O_5 \cdot 0.5H_2O$ (1054.66): calcd. C 80.86, H 10.80; found C 80.87, H 11.02.

Compound Y2: This compound was prepared from **15** (200 mg, 0.09 mmol), DIBAL-H (0.23 mL), in THF (14 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **Y2** (86.00 mg, 43%). Orange glassy product. IR (KBr): $\tilde{\nu}$ = 3212 (–OH), 2151 (C≡C) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.77 (s, 2 H), 7.49–7.58 (m, 7 H), 7.13 (d, J = 7 Hz, 4 H), 7.04 (dd, J = 7 and 2 Hz, 4 H), 6.80 (d, J = 8 Hz, 2 H), 6.74 (d, J = 8 Hz, 2 H), 4.74 (s, 2 H), 4.00 (t, J = 7 Hz, 4 H), 3.87 (m, 12 H), 1.78 (m, 16 H), 1.28–1.57 (m, 144 H), 0.89 (m, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 149.9, 149.8, 148.8, 148.687 141.3, 134.4, 131.9, 131.5, 130.7, 130.4, 129.9, 126.7, 126.5, 125.95, 125.9, 125.8, 125.1, 125.0, 124.8, 122.6, 122.5, 116.5, 116.45, 115.2, 115.1, 113.0, 95.9, 94.7, 93.1, 92.9, 90.2, 86.9, 86.1, 69.1, 69.0, 68.9, 64.5, 31.9, 31.6, 29.7, 29.5, 29.45, 29.4, 29.3, 26.1, 26.1, 22.7, 14.1, 13.9 ppm. $C_{151}H_{224}O_9$ (2183.39): calcd. C 83.05, H 10.35; found C 83.07, H 10.33.

General Procedure for the Preparation of C_{60}-G1, C_{60}-G2, C_{60}-Y1, and C_{60}-Y2: A solution of the appropriate benzaldehyde, C_{60}, and *N*-methylglycine in toluene was refluxed under argon for 24 h. After cooling, the resulting solution was evaporated to dryness. The product was then purified as outlined in the following text.

Compound C_{60}-G1: This compound was prepared from **4** (50 mg, 0.48 mmol), C_{60} (380 mg, 0.53 mmol), *N*-methylglycine (346 mg, 0.53 mmol) in toluene (225 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **C_{60}-G1** (522 mg, 61%). Brown glassy product. IR (KBr): $\tilde{\nu}$ = 2157 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_2$, 110 °C): δ = 7.98 (d, J = 1 Hz, 2 H), 7.66 (t, J = 2 Hz, 1 H), 7.11 (dd, J = 2 and 8 Hz, 2 H), 7.06 (d, J = 2 Hz, 2 H), 6.83 (d, J = 8 Hz, 2 H), 5.00 (d, J = 10 Hz, 1 H), 4.90 (s, 1 H), 4.27 (d, J = 10 Hz, 1 H), 4.01 (t, J = 7 Hz, 8 H), 2.83 (s, 3 H), 1.83 (2t, J = 7 Hz, 8 H), 1.27–1.47 (m, 72 H), 0.89 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 146.0, 145.95, 145.9, 145.7, 145.6, 145.5, 145.35, 145.3, 145.2, 145.1, 144.6, 144.5, 144.3, 143.0, 142.9, 142.7, 142.5, 142.25, 142.2, 142.1, 142.0, 141.95, 141.9, 141.6, 140.1, 139.6, 137.7, 137.0, 136.5, 135.9, 135.6, 134.5, 125.1, 116.6, 114.9, 113.2, 90.9, 87.1, 82.9, 69.9, 69.2, 69.1, 69.0, 40.1, 31.9, 29.7, 29.6, 29.4, 29.3, 29.2, 29.15, 26.0, 25.95, 22.7, 14.1 ppm. FAB-MS: 1791.6 (60%, $[M]^+$, calcd. for $C_{133}H_{115}O_4N$ 1791.4), 1070.9 (100%, $[M - C_{60}]^+$, calcd. for $C_{73}H_{115}O_4N$ 1070.7). $C_{133}H_{115}O_4N$ (1791.34): calcd. C 89.17, H 6.47, N 0.78; found C 88.78, H 6.55, N 0.45.

Compound C_{60}-G2: This compound was prepared from **10** (500 mg, 0.23 mmol), C_{60} (182 mg, 0.25 mmol), *N*-methylglycine (165 mg, 1.86 mmol) in toluene (180 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **C_{60}-G2** (352 mg, 52%). Brown glassy product. IR (KBr): $\tilde{\nu}$ = 2152 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, –10 °C): δ = 8.18 (s, 1 H), 7.67 (t, J = 2 Hz, 1 H), 7.63 (s, 7 H), 7.09 (dd, J = 2 and 6 Hz, 4 H), 7.03 (d, J = 2 Hz, 4 H), 6.83 (d, J = 8 Hz, 4 H), 5.02 (d, J = 10 Hz, 1 H), 4.93 (s, 1 H), 4.25 (d, J = 10 Hz, 1 H), 4.01 (2t, J = 7 Hz, 16 H), 2.85 (s, 3 H), 1.88 (m, 16 H), 1.48 (m, 144 H), 0.89 (2t, J = 7 Hz, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.2, 145.15, 145.1, 145.05, 144.6, 144.5, 144.3, 143.0, 142.9, 142.6, 142.5, 142.2, 142.1, 142.0, 141.9, 141.85, 141.6, 141.5, 140.1, 139.6, 138.2, 137.1, 136.5, 135.9, 135.6, 135.0, 134.0, 133.7, 125.1, 124.4, 123.4, 116.6, 114.8, 113.2, 91.2, 89.3, 86.4, 82.6, 69.8, 69.2, 69.1, 68.9, 40.0, 31.9, 31.7, 29.7, 29.6, 29.4, 29.35, 29.2, 29.15, 26.1, 26.0, 22.7, 22.4, 14.1 ppm. MALDI-TOF-MS: 2930.3 (9%, $[M]^+$, calcd. for $C_{213}H_{228}O_8N$: 2930.2), 2208.6 (100%, $[M - C_{60}]^+$, calcd. for $C_{153}H_{227}O_8N$ 2208.5), 720.0 (100%, $[C_{60}]^+$, calcd. for C_{60} 720.0). $C_{213}H_{227}O_8N$ (2929.08): calcd. C 87.34, H 7.81, N 0.48; found C 86.61, H 7.85, N 0.61.

Compound C_{60}-Y1: This compound was prepared from **5** (350 mg, 0.34 mmol), C_{60} (266 mg, 0.37 mmol), *N*-methylglycine (242 mg, 2.71 mmol) in toluene (200 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **C_{60}-Y1** (275 mg, 46%). Brown glassy product. IR (KBr): $\tilde{\nu}$ = 2157 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_2$, 90 °C): δ = 8.02 (d, J = 2 Hz, 1 H), 7.82 (dd, J = 2 and 8 Hz, 1 H), 7.62 (d, J = 8 Hz, 1 H), 7.13 (2dd, J = 2 and 8 Hz, 2 H), 7.08 (d, J = 2 Hz, 1 H), 7.03 (d, J = 2 Hz, 1 H), 6.80 (2d, J = 8 Hz, 2 H), 5.00 (d, J = 10 Hz, 1 H), 4.92 (s, 1 H), 4.28 (d, J = 10 Hz, 1 H), 3.99 (2t, J = 7 Hz, 4 H), 3.87 (2t, J = 7 Hz, 4 H), 2.83 (s, 3 H), 1.79 (m, 8 H), 1.26–1.44 (m, 72 H), 0.89 (m, 12 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.1, 142.05, 142.0, 141.95, 141.9, 141.8, 141.6, 141.5, 140.0, 139.9, 139.6, 136.9, 136.85, 136.4, 135.9, 135.6, 131.7, 128.5, 126.2, 124.9, 124.8, 116.4, 115.2, 113.0, 94.9, 94.7, 87.1, 86.9, 82.9, 69.9, 69.0, 68.9, 68.8, 40.0, 32.1, 31.9, 31.7, 29.7, 29.65, 29.6, 29.5, 29.45, 29.4, 29.35, 29.3, 29.2, 26.1, 26.05, 26.0, 22.9, 22.7, 22.4, 14.1 ppm. FAB-MS: 1791 (19%, $[M]^+$, calcd. for $C_{133}H_{115}O_4N$: 1791.4), 1070.6 (100%, $[M - C_{60}]^+$, calcd. for $C_{73}H_{115}O_4N$ 1070.7). $C_{133}H_{115}O_4N$ (1791.34): calcd. C 89.17, H 6.47, N 0.78; found C 88.78, H 6.55, N 0.45.

Compound C_{60}-Y2: This compound was prepared from **15** (500 mg, 0.23 mmol), C_{60} (182 mg, 0.25 mmol), *N*-methylglycine (165 mg, 1.86 mmol) in toluene (180 mL). Column chromatography (SiO_2, hexane/CH_2Cl_2, 7:3) yielded **C_{60}-Y2** (337 mg, 50%). Brown glassy product. IR (KBr): $\tilde{\nu}$ = 2151 (C≡C) cm^{-1}. ^1H NMR (400 MHz, $C_2D_2Cl_2$, 110 °C): δ = 8.10 (s, 1 H), 7.91 (d, J = 8 Hz, 1 H), 7.82 (d, J = 2 Hz, 1 H), 7.79 (d, J = 2 Hz, 1 H), 7.70 (d, J = 8 Hz, 1 H), 7.53 (m, 2 H), 7.49 (dd, J = 2 and 8 Hz, 2 H), 7.17 (dd, J = 2 and 8 Hz, 4 H), 7.12 (dd, J = 2 and 5 Hz, 4 H), 6.87 (d, J = 8 Hz, 2 H), 6.83 (d, J = 8 Hz, 2 H), 5.00 (d, J = 10 Hz, 1 H), 4.93 (s, 1 H), 4.25 (d, J = 10 Hz, 1 H), 3.99 (t, J = 7 Hz, 8 H), 3.86 (m, 8 H), 2.81 (s, 3 H), 1.76 (m, 16 H), 1.27 (m, 144 H), 0.89 (2t, J = 7 Hz, 24 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 145.3, 145.25, 145.2, 145.1, 144.7, 144.6, 144.4, 143.1, 142.9, 142.7, 142.5, 142.2, 142.1, 142.0, 141.9, 141.65, 141.6, 140.2, 139.7, 137.8, 137.0, 136.4, 135.9, 135.6, 134.5, 134.4, 131.5, 130.4, 126.5, 126.0, 125.7, 125.1, 125.0, 122.4, 116.5, 115.2, 115.1, 113.0, 96.1, 94.8, 93.7, 93.6, 90.1, 86.9, 86.1, 82.9, 76.6, 69.9, 69.1, 69.0, 68.9, 40.0, 31.9, 29.7, 29.5, 29.45, 29.4, 29.3, 26.1, 26.0, 22.7, 14.1 ppm. MALDI-TOF-MS: 2229.6 (7%, $[M]^+$, calcd. for $C_{213}H_{227}O_8N$: 2229.2), 2208.7 (100%, $[M - C_{60}]^+$, calcd. for $C_{153}H_{227}O_8N$ 2208.5). $C_{213}H_{227}O_8N$ (2929.08): calcd. C 87.34, H 7.81, N 0.48; found C 87.45, H 7.92, N 0.07.

Electrochemistry: The electrochemical experiments were carried out in argon-purged CH_2Cl_2 solutions at 298 K with an EcoChemie Autolab 30 multipurpose instrument interfaced to a personal computer. In the cyclic voltammetry (CV) the working electrode was a glassy carbon electrode (0.08 cm^2, Amel) or a Pt disk ultramicroelectrode (r = 25 μm). In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and a silver wire was employed as a quasi-reference electrode (AgQRE). The potentials reported are referred to SCE by measuring the AgQRE potential with respect to ferrocene. The concentration of the compounds examined was of the order of 5×10^{-4} M; 0.05 M tetrabutylammonium hexafluoro-phosphate ($TBAPF_6$) was added as supporting electrolytes. Cyclic voltammograms were obtained with scan rates in the range 0.05–20 V s^{-1}.

Photophysics: The photophysical investigations were carried out in CH_2Cl_2 (Carlo–Erba, spectrofluorimetric grade). The samples were placed in fluorimetric 1-cm path cuvettes. Absorption spectra were recorded with a Perkin–Elmer λ40 spectrophotometer. Uncorrected emission spectra were obtained with a Spex Fluorolog II spectrofluorimeter (continuous 150-W Xe lamp), equipped with a Hamamatsu R-928 photomultiplier tube. The corrected spectra were obtained via a calibration curve. Fluorescence quantum yields obtained from spectra on an energy scale [cm^{-1}] were measured with the method described by Demas and Crosby[22] using as standards air equilibrated solutions of quinine sulfate in 1 N H_2SO_4 (Φ_{em} = 0.546).[23] Emission lifetimes on the nanosecond time scale were determined with an IBH single-photon counting spectrometer equipped with a thyratron gated nitrogen lamp working in the range 2–40 kHz (λ_{exc} = 337 nm, 0.5 ns time resolution); the detector was a red-sensitive (185–850 nm) Hamamatsu R-3237-01 photomultiplier tube. Experimental uncertainties are estimated to be 8% for lifetime determinations, 20% for emission quantum yields, and 1 nm and 5 nm for absorption and emission peaks respectively.

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[1] G. R. Newkome, C. N. Moorefield, F. Vögtle, *Dendrimers and Dendrons: Concepts, Syntheses, Applications*, VCH, Weinheim, **2001**.

[2] D. M. Guldi, A. Swartz, C. P. Luo, R. Gomez, J. L. Segura, N. Martin, *J. Am. Chem. Soc.* **2002**, *124*, 10875–10886.

[3] J. S. Moore, Z. Xu, *Macromolecules* **1991**, *24*, 5893–5894; J. S. Moore, Z. Xu, *J. Am. Chem. Soc.* **1994**, *116*, 4537–4550; J. S. Moore, Z. Xu, *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 246–248.

[4] Z. Peng, Y. Pan, B. Xu, J. Zhang, *J. Am. Chem. Soc.* **2000**, *122*, 6619–6623.

[5] J.-F. Nierengarten, S. Zhang, A. Gégout, M. Urbani, N. Armaroli, G. Marconi, Y. Rio, *J. Org. Chem.* **2005**, *70*, 7550–7557.

[6] J. S. Moore, *Acc. Chem. Res.* **1997**, *30*, 402–413.

[7] C. Devadoss, P. Bharathi, J. S. Moore, *J. Am. Chem. Soc.* **1996**, *118*, 9635–9644; Y. Pan, M. Lu, Z. Peng, J. S. Melinger, *J. Org. Chem.* **2003**, *68*, 6952–6958.

[8] N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, *Chem. Commun.* **2000**, 599–600; G. Accorsi, N. Armaroli, J.-F. Eckert, J.-F. Nierengarten, *Tetrahedron Lett.* **2002**, *43*, 65–68; J.-F. Nierengarten, N. Armaroli, G. Accorsi, Y. Rio, J.-F. Eckert, *Chem. Eur. J.* **2003**, *9*, 36–41; N. Armaroli, G. Accorsi, J. N. Clifford, J.-F. Eckert, J.-F. Nierengarten, *Chem. Asian J.* **2006**, *1*, 564–574.

[9] F. Langa, M. J. Gomez-Escalonilla, E. Diez-Barra, J. C. Garcia-Martinez, A. de la Hoz, J. Rodriguez-Lopez, A. Gonzalez-Cortes, V. Lopez-Arza, *Tetrahedron Lett.* **2001**, *42*, 3435–3438; J. L. Segura, R. Gomez, N. Martin, C. P. Luo, A. Swartz, D. M. Guldi, *Chem. Commun.* **2001**, 707–708; M. Schwell, N. K. Wachter, J. H. Rice, J. P. Galaup, S. Leach, R. Taylor, R. V. Bensasson, *Chem. Phys. Lett.* **2001**, *339*, 29–35; L. Pérez, J. C. Garcia-Martinez, E. Diez-Barra, P. Atienzar, H. Garcia, J. Rodriguez-Lopez, F. Langa, *Chem. Eur. J.* **2006**, *12*, 5149–5157.

[10] V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, *Acc. Chem. Res.* **1998**, *31*, 26–34; V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero, S. Serroni, *Coord. Chem. Rev.* **2001**, *219*, 545–572; A. Adronov, J. M. J. Frechet, *Chem. Commun.* **2000**, 1701–1710; M. Fischer, F. Vögtle, *Angew. Chem. Int. Ed.* **1999**, *38*, 885–905.

[11] J. Baffreau, L. Perrin, S. Leroy-Lhez, P. Hudhomme, *Tetrahedron Lett.* **2005**, *46*, 4599–4603; J.-F. Nierengarten, *New J. Chem.* **2004**, *28*, 1177–1191; J.-F. Nierengarten, *Sol. Energy Mater. and Sol. Cells* **2004**, *83*, 187–199.

[12] P. L. Burn, S.-C. Lo, I. D. W. Samuel, *Adv. Mater.* **2007**, *19*, 1675–1688.

[13] N. Armaroli, in *Fullerenes: from synthesis to optoelectronic properties* (Eds.: D. M. Guldi, N. Martin), Kluwer Academic Publishers, Dordrecht, **2002**, pp. 137–162.

[14] *Metal-catalyzed Cross-coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**.

[15] M. Prato, M. Maggini, *Acc. Chem. Res.* **1998**, *31*, 519–526.

[16] F. Ajamaa, T. M. Figueira Duarte, C. Bourgogne, M. Holler, P. W. Fowler, J.-F. Nierengarten, *Eur. J. Org. Chem.* **2005**, 3766–3774.

[17] E. J. Corey, P. L. Fuchs, *Tetrahedron Lett.* **1972**, *13*, 3769–3772.

[18] M. Goez, G. Eckert, *J. Phys. Chem.* **1991**, *95*, 1179.

[19] J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, S.-G. Liu, L. Echegoyen, F. Barigelletti, N. Armaroli, L. Ouali, V. Krasnikov, G. Hadziioannou, *J. Am. Chem. Soc.* **2000**, *122*, 7467–7479; N. Armaroli, G. Accorsi, J.-P. Gisselbrecht, M. Gross, V. Krasnikov, D. Tsamouras, G. Hadziioannou, M. J. Gomez-Escalonilla, F. Langa, J.-F. Eckert, J.-F. Nierengarten, *J. Mater. Chem.* **2002**, *12*, 2077–2087.

[20] J. N. Clifford, T. Gu, J.-F. Nierengarten, N. Armaroli, *Photochem. Photobiol. Sci.* **2006**, *5*, 1165–1172.

[21] T. M. Figueira-Duarte, A. Gégout, J.-F. Nierengarten, *Chem. Commun.* **2007**, 109–119.

[22] J. N. Demas, G. A. Crosby, *J. Phys. Chem.* **1971**, *75*, 991.

[23] S. R. Meech, D. Phillips, *J. Photochem.* **1983**, *23*, 193–217.

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