Available online at www.sciencedirect.com
ScienceDirect
C. R. Chimie 12 (2009) 479–488
COMPTES RENDUS CHIMIE
http://france.elsevier.com/direct/CRAS2C/

Full paper / Mémoire

Synthesis of isomeric phenyleneethynylene dendrons and their incorporation in fullerene-based dyads

Michel Holler, Maxence Urbani, Aline Gégout, Sheng Zhang, Jean-François Nierengarten*

Laboratoire de chimie des matériaux moléculaires, Université Louis-Pasteur et CNRS (UMR 7509), École européenne de chimie, polymères et matériaux (ECPM), 25, rue Becquerel, 67087 Strasbourg cedex 2, France

Received 2 October 2008; accepted after revision 27 October 2008
Available online 4 December 2008

Abstract

Two series of isomeric dyads with differently branched phenyleneethynylene-based moieties and a pyrrolidinofullerene core have been prepared. The synthetic approach to prepare these compounds relies upon the 1,3-dipolar cycloaddition of an azomethine ylide generated in situ from the corresponding aldehydes and *N*-methylglycine. ***To cite this article: M. Holler et al., C. R. Chimie 12 (2009).***

Keywords: Fullerene; Terminal alkyne; Cross-coupling reaction; Dibromoolefination; Conjugated systems

1. Introduction

Dendrimers with a π-conjugated backbone have generated significant research efforts in the past years [1]. The electronic properties of such compounds 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 make them attractive photoactive components for the preparation of new 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]. Among the various terminal energy acceptors used in such light harvesting systems, [60] fullerene ($\mathbf{C_{60}}$) has proven to be particularly interesting [8,9]. Effectively, its first singlet and triplet excited-states are relatively low in energy and photo-induced energy transfer events have been evidenced in numerous fullerene-based dyads [11]. In this article, we report the synthesis of fullerene derivatives functionalized with isomeric phenyleneethynylene-based dendrons possessing 1,3,5-triethynylbenzene or 1,2,4-triethynylbenzene branching units (Fig. 1). Whereas the π-conjugation of the dendritic antenna in $\mathbf{C_{60}}$-**G1** and $\mathbf{C_{60}}$-**G2** is rather limited due to the all-*meta*-branching scheme, the dendritic scaffold of $\mathbf{C_{60}}$-**Y1** and $\mathbf{C_{60}}$-**Y2** exhibits an increase of the conjugation

* Corresponding author.
E-mail address: nierengarten@chimie.u-strasbg.fr (J.-F. Nierengarten).

1631-0748/$ - see front matter © 2008 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.crci.2008.10.011

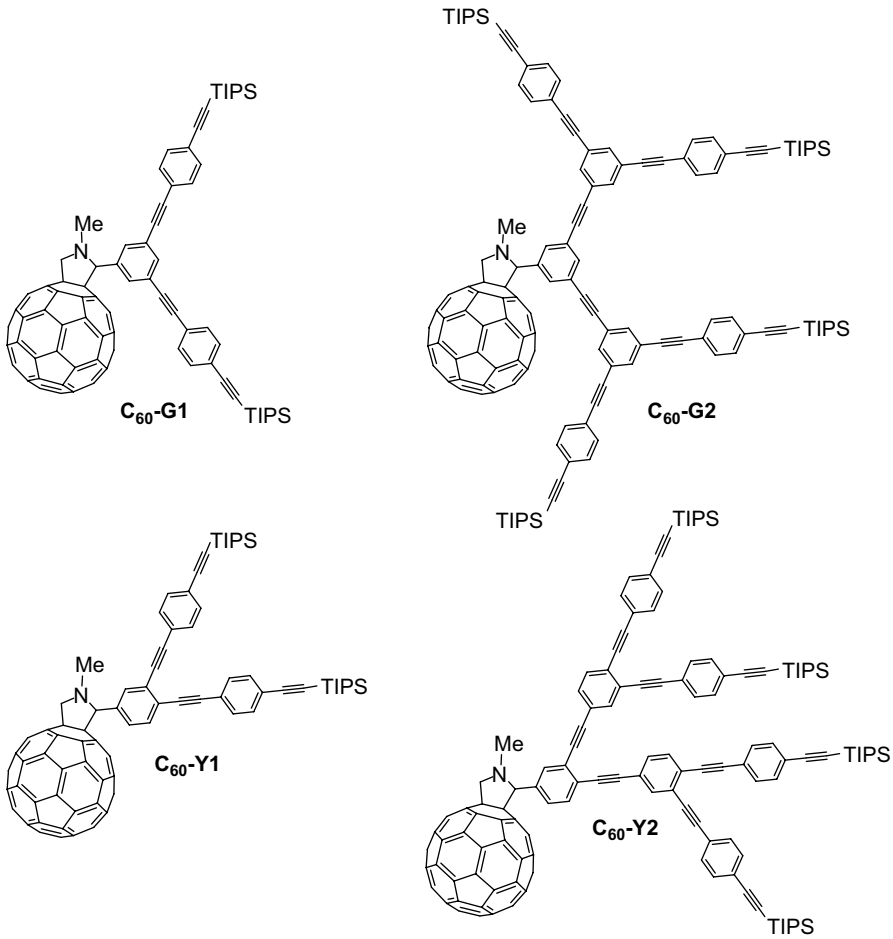


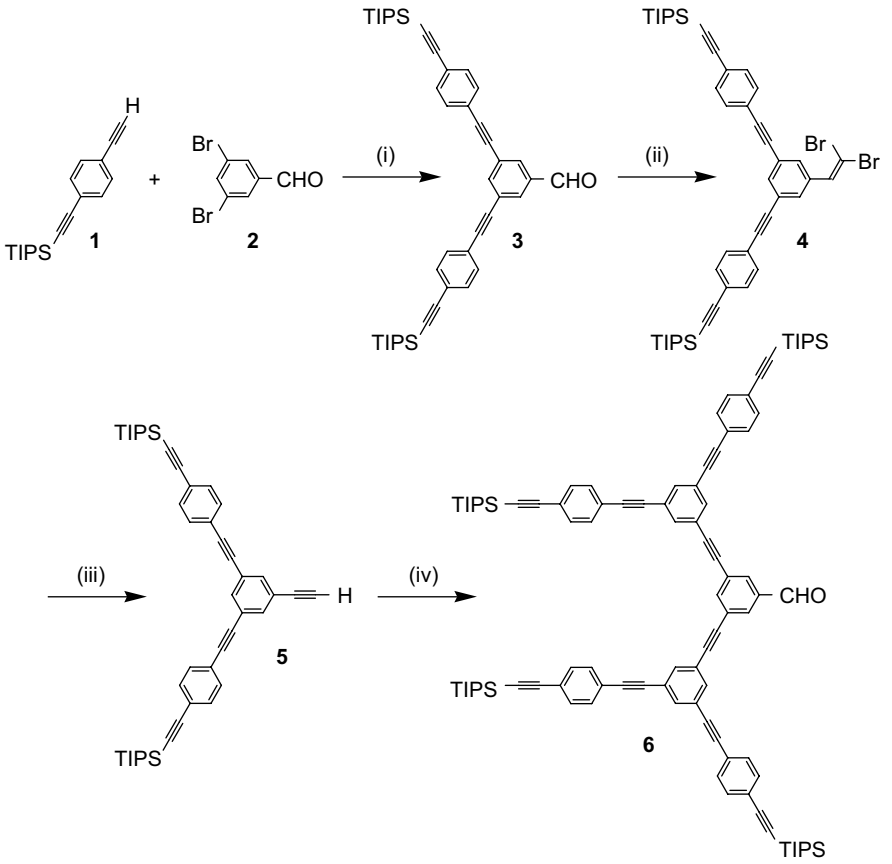
Fig. 1. Compounds $\mathbf{C_{60}}$-**Gn** and $\mathbf{C_{60}}$-**Yn** (***n*** = 1 or 2; TIPS = triisopropylsilyl).

length when going from the first to the second generation compound.

2. Results and discussion

The synthetic approach to prepare compounds $\mathbf{C_{60}}$-**G*n*** and $\mathbf{C_{60}}$-**Y*n*** (***n*** = 1 or 2) relies upon the 1,3-dipolar cycloaddition of an azomethine ylide generated in situ from the corresponding aldehydes and *N*-methylglycine. This methodology has proven to be a powerful procedure for the functionalization of $\mathbf{C_{60}}$ due to its versatility and the ready availability of the starting materials [12]. The synthesis of dendrons **3** and **6**, the key building blocks for the synthesis of $\mathbf{C_{60}}$-**G1** and $\mathbf{C_{60}}$-**G2**, respectively, is shown in Scheme 1. Reaction of 3,5-dibromobenzaldehyde (**2**) with mono-protected bisalkyne **1** [5] under Sonogashira conditions gave the first generation dendron **3** in 85% yield. Dibromoolefination according to Corey–Fuchs [13] then provided **4,** which, after treatment with an excess of LDA in THF at −78 °C and quenching with NH_4Cl, afforded terminal alkyne **5**. Compound **5** was subjected to a Pd-catalyzed cross-coupling reaction with **2** to yield the second generation dendron **6**.

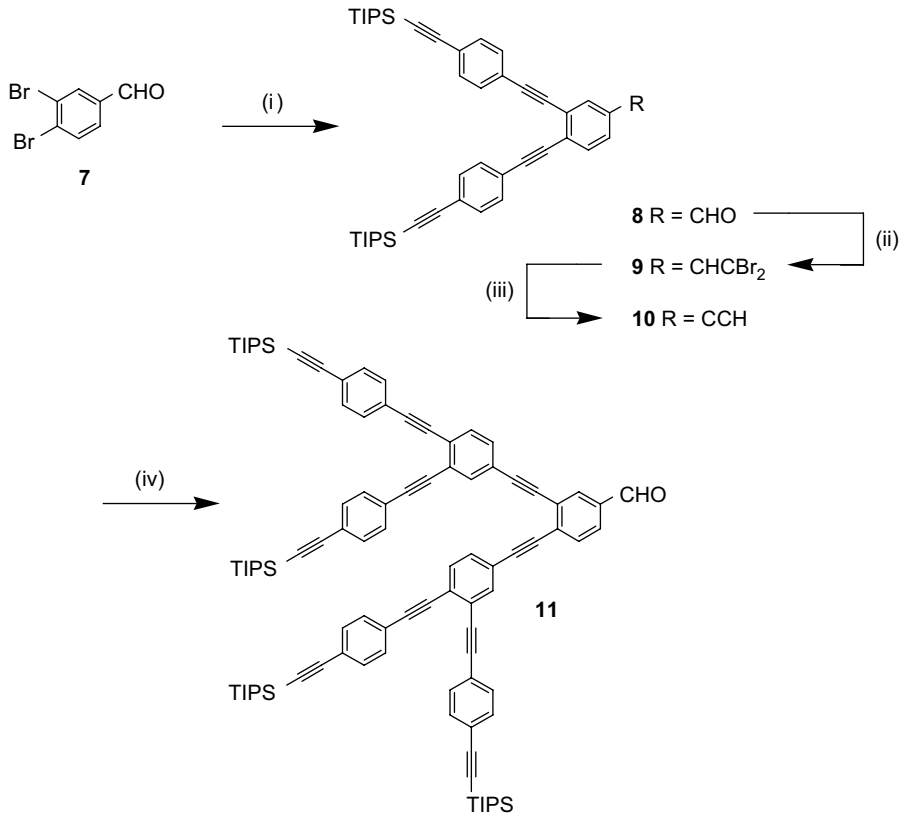
Compounds **8** and **11** were obtained from 3,4-dibromobenzaldehyde (**7**) by following a similar synthetic approach as that described above for the preparation of the corresponding isomers **3** and **6** (Scheme 2). Pd-catalyzed cross-coupling reaction of terminal alkyne **1** with 3,4-dibromobenzaldehyde (**7**), Corey–Fuchs dibromoolefination and treatment with an excess of LDA gave **10** in an overall 87% yield. Subsequent Sonogashira coupling with **7** yielded the second generation dendron **11**. It is worth mentioning here that the methodology based on successive Sonogashira coupling reactions of a terminal alkyne with a halobenzaldehyde, Corey–Fuchs dibromoolefination and treatment with LDA was also successfully applied



Scheme 1. Reagents and conditions: (i) $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (85%); (ii) CBr_4, PPh_3, Zn dust, CH_2Cl_2 (68%); (iii) LDA, THF then NH_4Cl, H_2O (71%); (iv) **2**, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (30%).

to the synthesis of linear oligophenyleneethynylene derivatives [14]. It is an interesting alternative to the approaches reported by the groups of Tour [15] and Godt [16]. On the one hand, compared to the strategy based on the trimethylsilyl and the 3,3-diethyltriazene functions as complementary protecting groups for terminal alkyne and aryl iodine, respectively, it avoids the use of large amounts of rather volatile carcinogenic methyl iodide [15]. On the other hand, compared to the strategy based on the bromine–iodine selectivity of the Pd-catalyzed alkyne–aryl coupling which is not always completely iodo-selective, it prevents the formation of undesirable symmetric by-products [16].

Owing to the presence of the triisopropylsilyl (TIPS) substituents, dendrons **3**–**6** and **8**–**11** are highly soluble in common organic solvents (CH_2Cl_2, $CHCl_3$, THF), and ^{1}H- and ^{13}C NMR spectroscopic characterization was easily achieved. The ^{1}H NMR spectra of compounds **3** and **6** recorded in $CDCl_3$ are shown in Fig. 2. For both compounds, the resonance arising from the aldehydic proton is observed at ca. 10 ppm. In the aromatic region, the spectrum of **3** shows two sets of signals in a typical pattern for a 3,5-disubstituted benzaldehyde moiety as well as a singlet at 7.50 ppm for the protons of the two *para*-disubstituted phenyl groups. The ^{1}H NMR of **6** is also in full agreement with the proposed structure. In addition to the signals corresponding to the protons of the central 3,5-diethynylbenzaldehyde moiety, the resonances arising from the two equivalent 1,3,5-triethynylbenzene units are observed at 7.68 ppm. The ^{1}H NMR spectra of **8** and **11** recorded in $CDCl_3$ are depicted in Fig. 3. When compared to the spectra of **3** and **6** shown in Fig. 2, the spectra of **8** and **11** are more complicated due to their reduced symmetry resulting from the 1,3,4-branching motif. In the aromatic region, the ^{1}H NMR spectrum of **8** is characterized by three sets of signals for the aromatic protons of the central 1,3,4-trisubstituted phenyl ring (H_a, H_b and H_c) as well as a pseudo-singlet for the protons of the two *para*-disubstituted phenyl groups. The ^{1}H NMR spectrum of **11** is also consistent with the proposed structure. In



Scheme 2. Reagents and conditions: (i) **1**, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (75%); (ii) CBr_4, PPh_3, Zn dust, CH_2Cl_2 (95%); (iii) LDA, THF then NH_4Cl, H_2O (92%); (iv) **7**, $PdCl_2(PPh_3)_2$, CuI, PPh_3, Et_3N, THF (78%).

addition to the signals corresponding to the protons of the central 3,4-diethynylbenzaldehyde moiety, the resonances arising from the two 1,3,4-triethynylbenzene units appear as a single set of three signals. These two aromatic rings are in principle non-equivalent, however both benzene rings are substituted by three alkyne groups and must be in a similar chemical environment; they are therefore pseudo-equivalent. Finally, the peaks of the peripheral *para*-diethynyl phenyl moieties appear between 7.44 and 7.47 ppm. Compounds **3**–**6** and **8**–**11** were further characterized by IR spectroscopy. For all the derivatives, the characteristic C≡C stretching band is observed at 2151–2152 cm^{-1}. In the IR spectrum of **3**, **6**, **8** and **11** the diagnostic aldehyde band is observed at ca. 1700 cm^{-1}. In the case of **5** and **10**, the C–H stretching band characteristic of the terminal alkyne function is seen at ca. 3300 cm^{-1}.

Reaction of aldehydes **3**, **6**, **8** and **11** with *N*-methylglycine and $\mathbf{C_{60}}$ in refluxing toluene gave the corresponding pyrrolidinofullerene $\mathbf{C_{60}}$-G***n*** and $\mathbf{C_{60}}$-Y***n*** (***n*** = 1 or 2) in 27–52% isolated yield (Scheme 3). The structure of fullerodendrimers $\mathbf{C_{60}}$-G***n*** and $\mathbf{C_{60}}$-Y***n*** (***n*** = 1 or 2) was confirmed by analytical and spectroscopic data. The ^{1}H NMR spectra of $\mathbf{C_{60}}$-G***n*** and $\mathbf{C_{60}}$-Y***n*** (***n*** = 1 or 2) recorded in $CDCl_3$ exhibit the expected features with the signals arising from the dendritic branches, two doublets and a singlet for the pyrrolidine protons as well as a singlet for the N–CH_3 group. It is also important to note that the signals corresponding to the protons of the phenyl group directly attached to the pyrrolidine ring are broad at room temperature. As previously described for phenylpyrrolidinofullerene derivatives [17], this indicates restricted rotation of the phenyl substituent on the pyrrolidine ring. This was confirmed by variable-temperature NMR studies showing a clear coalescence and a reversible narrowing of all the peaks for all the compounds. Indeed, the ^{1}H NMR spectra of $\mathbf{C_{60}}$-G***n*** and $\mathbf{C_{60}}$-Y***n*** (***n*** = 1 or 2) recorded at high temperature (90–120 °C) are all well resolved, with sharp signals for the protons of the aromatic substituent attached to the pyrrolidine ring. The ^{13}C NMR spectra of $\mathbf{C_{60}}$-G***n*** and $\mathbf{C_{60}}$-Y***n*** (***n*** = 1 or 2) were also in full agreement

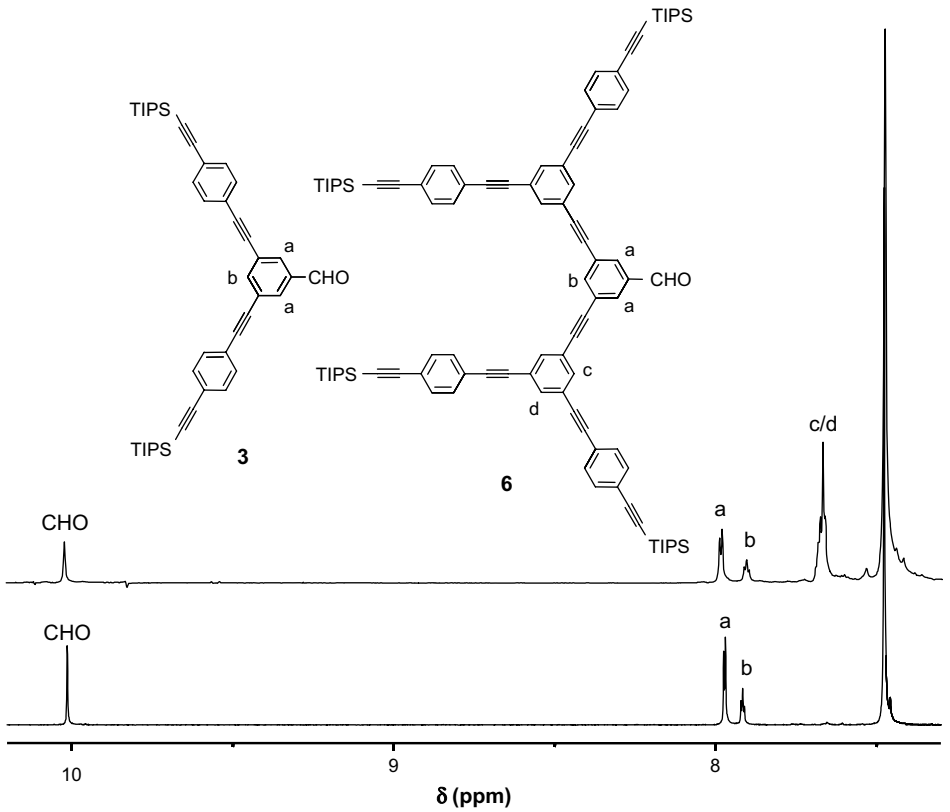


Fig. 2. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of compounds **3** (bottom) and **6** (top).

with their C_1 symmetry resulting from the presence of the asymmetric C atom in the pyrrolidine ring. Finally, the structure of fullerodendrimers **C_{60}-G*n*** and **C_{60}-Y*n*** (***n*** = 1 or 2) was confirmed by mass spectrometry. As a typical example, the FAB mass spectrum of compound **C_{60}-G2** is shown in Fig. 4. The expected molecular ion peak is observed at 2176.4. Two characteristic fragments are also observed at 1455.1 and 720.0 corresponding to $[M - \mathbf{C_{60}}]^+$ and $[\mathbf{C_{60}}]^+$, respectively. However, no signals corresponding to defected dendrimers could be detected, thus showing the monodispersity of **C_{60}-G2**.

3. Conclusion

Two series of isomeric dyads with differently branched phenyleneethynylene-based moieties and a pyrrolidinofullerene core have been prepared. Preliminary luminescence measurements reveal no emission from the π-conjugated dendritic branches in **C_{60}-G*n*** and **C_{60}-Y*n*** (***n*** = 1 or 2) thus indicating a strong quenching of the phenyleneethynylene fluorescence by the fullerene moiety in all compounds. Detailed photophysical studies are currently under investigation to elucidate the nature of the intramolecular photo-induced processes in **C_{60}-G*n*** and **C_{60}-Y*n*** (***n*** = 1 or 2).

4. Experimental section

4.1. General

Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over sodium benzophenone ketyl. Compounds **1** and **8**–**11** [5] were prepared according to previously reported procedures. 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

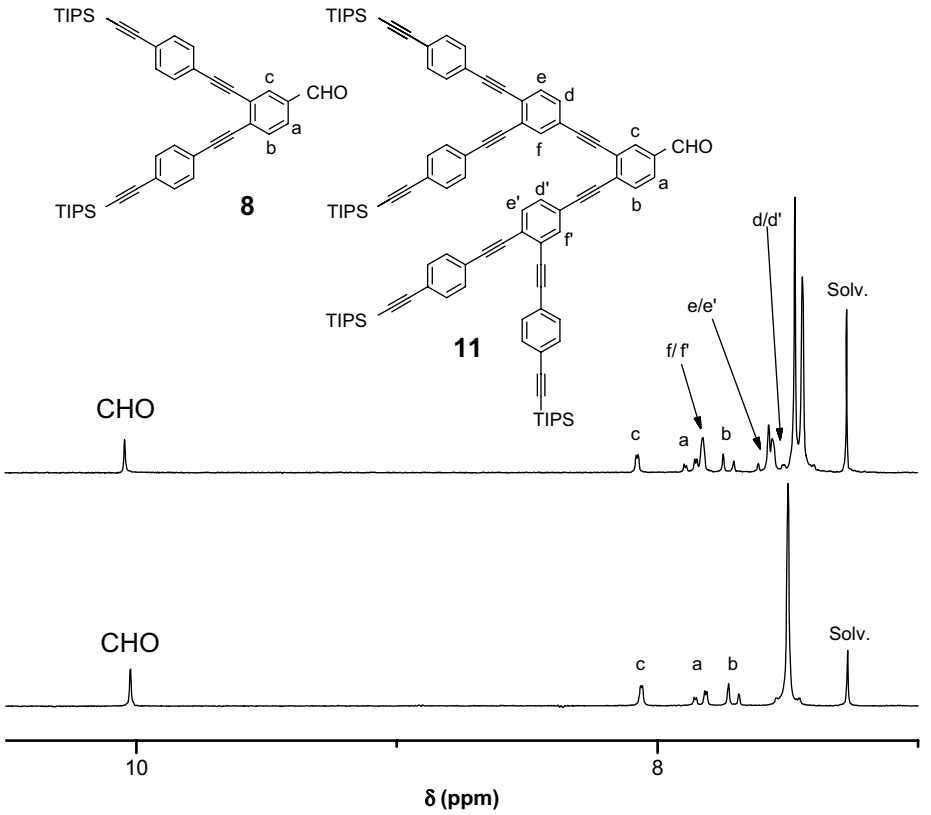
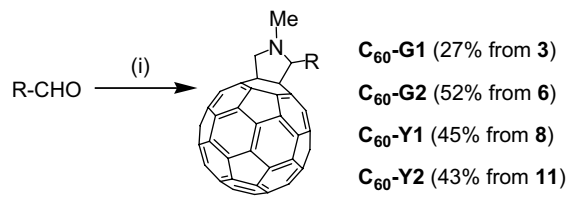


Fig. 3. ^{1}H NMR spectra (300 MHz, $CDCl_3$) of compounds **8** (bottom) and **11** (top).

Mattson Genesis Series FTIR instrument. NMR spectra were recorded on a Bruker AC 200 or AC 400 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. Elemental analyses were performed by the analytical service at the Institut Charles Sadron, Strasbourg.

4.2. General procedure for the Sonogashira cross-coupling reactions

To an oven dried glass screw capped tube were added all solids including the aryl bromide, 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 conducted 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 filtered through a plug of SiO_2 (CH_2Cl_2). The solvent was evaporated and the product purified as outlined in the following text.



Scheme 3. Reagents and conditions: (*i*) C_{60}, *N*-methylglycine, toluene, Δ.

*4.2.1. Compound **3***

This compound was prepared from **1** (4.0 g, 14.2 mmol), **2** (1.25 g, 4.73 mmol), $Pd(PPh_3)_2Cl_2$ (99.5 mg, 0.14 mmol), CuI (30.7 mg, 2 mmol) and PPh_3 (92 mg, 0.36 mmol) in a 4/1 THF/Et_3N mixture (40 mL). Column chromatography (SiO_2, Hexane/CH_2Cl_2 9:1) yielded **3** (2.68 g, 85%). Colorless oil. IR (KBr): 1705 (C═O), 2152 (C≡C). ^{1}H NMR ($CDCl_3$, 200 MHz): 10.01 (s, 1H), 7.97 (d, $J = 2$ Hz, 2H), 7.91 (t, $J = 2$ Hz, 1H), 7.48 (s, 8H), 1.09 (s, 42H). ^{13}C NMR ($CDCl_3$, 75 MHz): 190.6, 139.4, 136.7, 132.0, 131.9, 131.5, 124.7, 124.0, 122.2, 106.4, 93.3, 91.2, 88.8,

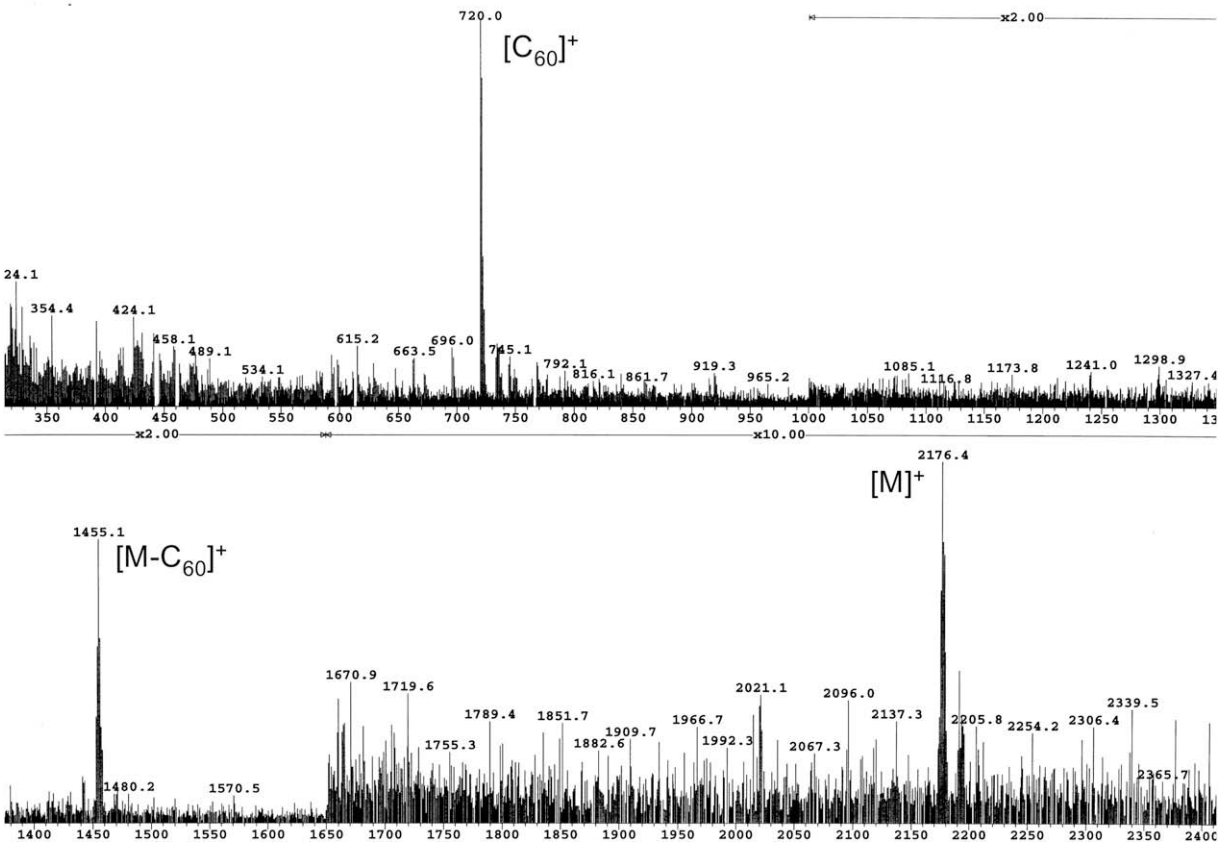


Fig. 4. FAB mass spectrum of compound **C_{60}-G2**.

18.6, 11.3. Anal. Calcd for $C_{45}H_{54}OSi_2$, 0.5 H_2O: C 80.90, H 8.30; found: C 80.44, H 8.29.

*4.2.2. Compound **6***

This compound was prepared from **5** (1.2 g, 1.81 mmol), **2** (0.19 g, 0.73 mmol), $Pd(PPh_3)_2Cl_2$ (16 mg, 0.02 mmol), CuI (5 mg, 0.04 mmol) and PPh_3 (23 mg, 0.09 mmol) in a 4/1 THF/Et_3N mixture (10 mL). Column chromatography (SiO_2, Hexane/CH_2Cl_2 8:2) yielded **6** (0.31 g, 30%). Yellow glassy solid. IR (neat): 1700 (C═O), 2150 (C≡C). ^1H NMR ($CDCl_3$, 300 MHz): 10.02 (s, 1H), 7.99 (d, $J = 2$ Hz, 2H), 7.90 (t, $J = 2$ Hz, 1H), 7.67 (m, 6H), 7.48 (s, 16H), 1.10 (s, 84H). ^{13}C NMR ($CDCl_3$, 75 MHz): 190.5, 139.6, 136.8, 134.6, 134.2, 132.3, 132.0, 131.5, 124.5, 124.1, 123.9, 123.3, 122.5, 106.5, 93.2, 90.6, 89.9, 89.3, 88.2, 18.7, 11.3. Anal. Calcd for $C_{99}H_{110}OSi_4$, 0.5 H_2O: C 82.73, H 7.78; found: C 82.56, H 8.10.

*4.2.3. Compound **8***

This compound was prepared from **1** (4.40 g, 15.57 mmol), **7** (1.53 g, 5.80 mmol), $Pd(PPh_3)_2Cl_2$ (0.49 g, 0.70 mmol), CuI (57 mg, 0.29 mmol) and PPh_3 (0.23 g, 0.88 mmol) in THF/Et_3N 4:1 (60 mL). Column chromatography (SiO_2, Hexane/CH_2Cl_2 4:1) yielded **8** (2.90 g, 75%). Yellow solid (mp. 178 °C). IR (KBr): 2152 (C≡C), 1702 (C═O). ^1H NMR (200 MHz, $CDCl_3$): 10.02 (s, 1H), 8.06 (d, $J = 2$ Hz, 1H), 7.83 (dd, $J = 7$ and 2 Hz, 1 H), 7.70 (d, $J = 7$ Hz), 7.50 (s, 4H), 1.15 (s, 42 H). ^{13}C NMR (50 MHz, $CDCl_3$): 189.9, 135.2, 132.8, 132.0, 131.9 (2C), 131.4, 131.3, 130.8, 128.0, 126.3, 124.1, 123.8, 122.4, 122.2, 106.4, 106.3, 97.0, 94.5, 93.2, 93.0, 89.4, 88.7, 18.6, 11.2. Anal. Calc. for $C_{45}H_{54}Si_2O$: C 81.02, H 8.16; found: C 80.74, H 8.19.

*4.2.4. Compound **11***

This compound was prepared from **10** (2.1 g, 3.17 mmol), **7** (0.31 g, 1.17 mmol), $Pd(PPh_3)_2Cl_2$ (99 mg, 0.14 mmol), CuI (12 mg, 0.059 mmol) and PPh_3 (46 mg, 0.18 mmol) in THF/Et_3N 4:1 (20 mL). Column chromatography (SiO_2, Hexane/CH_2Cl_2 4:1) yielded **11** (1.32 g, 78%). Yellow solid (mp. 150 °C). IR (KBr): 2151 (C≡C), 1704 (C═O). ^1H NMR

(200 MHz, $CDCl_3$): 10.04 (s, 1 H), 8.07 (d, $J = 2$ Hz, 1H), 7.87 (dd, $J = 7$ and 2 Hz, 1H), 7.82 (broad s, 2H), 7.72 (d, $J = 7$ Hz, 1H), 7.58 (d, $J = 7$ Hz, 2H), 7.53 (dd, $J = 7$ and 2 Hz, 2H), 7.47 (s, 8H), 7.44 (s, 8H), 1.15 (s, 42 H), 1.13 (s, 42 H). ^{13}C NMR (50 MHz, $CDCl_3$): 190.1, 135.3, 135.0, 134.9, 132.7, 132.0, 131.9, 131.4, 131.3, 130.9, 126.4, 126.0, 125.9, 125.7, 123.8, 123.6, 122.6, 122.3, 106.6, 96.6, 95.5, 95.4, 94.2, 94.15, 94.1, 93.1, 93.0, 92.95, 92.9, 90.2, 89.8, 89.6, 89.1, 89.0, 18.6, 11.3, 11.2. Anal. Calcd for $C_{99}H_{110}Si_4O$: C 83.25, H 7.76; found: C 83.34, H 7.71.

4.3. General procedure for the dibromoolefination reactions

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 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 evaporated. The product was then purified as outlined in the following text.

*4.4. Compound **4***

This compound was prepared from **3** (1.5 g, 2.25 mmol), CBr_4 (3.73 g, 11.3 mmol), PPh_3 (2.95 g, 11.3 mmol) and Zn dust (0.73 g, 11.3 mmol) in CH_2Cl_2 (50 mL) and column chromatography (SiO_2, Hexane/CH_2Cl_2 9:1) yielded **4** (1.26 g, 68%). Yellow oil. IR (KBr): 2152 (C≡C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.66 (t, $J = 2$ Hz, 1 H), 7.62 (d, $J = 2$ Hz, 2H), 7.47 (s, 8H), 7.43 (s, 1H), 1.15 (s, 42 H). Anal. Calcd for $C_{46}H_{54}Si_2Br_2$: C 67.14, H 6.61; found: C 67.11, H 6.69.

*4.4.1. Compound **9***

This compound was prepared from **8** (2.80 g, 4.20 mmol), CBr_4 (8.36 g, 25.20 mmol), PPh_3 (6.61 g, 25.20 mmol) and Zn dust (1.65 g, 25.20 mmol) in CH_2Cl_2 (200 mL) and column chromatography (SiO_2, hexane) yielded **9** (3.30 g, 95%). Pale yellow solid (mp. 140 °C). IR (KBr): 2151 (C≡C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.75 (d, $J = 2$ Hz, 1H), 7.57 (d, $J = 7$ Hz, 1H), 7.51(dd, $J = 7$ and 2 Hz, 1H), 7.48 (m, 8 H), 7.47 (s, 1H), 1.15 (s, 42 H). ^{13}C NMR (50 MHz, $CDCl_3$): 135.2, 134.8, 131.9, 131.6, 131.3, 127.8, 125.7, 125.5, 123.6, 122.88, 122.8, 106.6, 94.5, 93.7, 92.95, 92.9, 91.2, 90.0, 89.6, 18.6, 11.3. Anal. Calcd for $C_{46}H_{54}Si_2Br_2$: C 67.14, H 6.61; found: C 67.37, H 6.67.

4.5. General procedure for the preparation of alkynes from dibromoolefines

A solution of LDA in THF was slowly added to a solution of the appropriate dibromoolefine in THF at −78 °C. After 3 h, a saturated aqueous NH_4Cl solution was added. The reaction mixture was diluted with hexane, washed with water, dried with $MgSO_4$ and evaporated. The product was then purified as outlined in the following text.

*4.5.1. Compound **5***

This compound was prepared from **4** (1.26 g, 1.53 mmol) and LDA (6.11 mmol) in THF (40 mL) and column chromatography (SiO_2, Hexane/CH_2Cl_2 8:1) yielded **5** (720 mg, 71%). Yellow glassy solid. IR (KBr): 2152 (C≡C), 3304 (C≡C−H). ^{1}H NMR ($CDCl_3$, 300 MHz): 7.66 (t, $J = 2$ Hz, 1H), 7.60 (d, $J = 2$ Hz, 2H), 5.30 (s, 8H); 3.12 (s, 1H), 1.14 (s, 42H). ^{13}C NMR ($CDCl_3$, 75 MHz): 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. Anal. Calcd for $C_{46}H_{54}Si_2$, H_2O: C 81.13, H 8.30; found: C 81.15, H 8.28.

*4.6. Compound **10***

This compound was prepared from **9** (3.28 g, 3.98 mmol) and LDA (20 mmol) in THF (60 mL) and column chromatography (SiO_2, hexane/CH_2Cl_2 20:1) yielded **10** (2.40 g, 92%). Colorless solid (mp. 155 °C). IR (KBr): 3314 (≡C−H), 2151 (C≡C). ^{1}H NMR (200 MHz, $CDCl_3$): 7.63 (d, $J = 2$ Hz, 1H), 7.46 (s, 8H), 7.42 (d, $J = 7$ Hz, 1 H), 7.34 (dd, $J = 2$ and 7 Hz), 3.16 (s, 1H), 1.15 (s, 42H). ^{13}C NMR (50 MHz, $CDCl_3$): 135.1, 132.0, 131.6, 131.4, 125.85, 125.8, 123.75, 123.7, 122.8, 122.1, 106.6, 95.1, 93.9, 93.0, 92.9, 89.7, 89.1, 82.4, 79.5, 18.6, 11.3. Anal. Calcd for $C_{46}H_{54}Si_2$: C 83.32, H 8.21; found: C 82.99, H 8.24.

4.7. General procedure for the preparation of pyrrolidinofullerene

N-Methylglycine and the appropriate aldehyde were added to a solution of $\mathbf{C_{60}}$ in toluene under argon. The mixture was heated at 115 °C. After 24 h the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The product was then purified as outlined in the following text.

4.7.1. Compound ***C_{60}-G1***

This compound was prepared from *N*-methylglycine (542 mg, 6.08 mmol), **3** (500 mg, 0.75 mmol), **C_{60}** (595 mg, 0.83 mmol) in toluene (670 mL) and column chromatography (SiO_2, Hexane/CH_2Cl_2 8:2) yielded **C_{60}-G1** (287 mg, 27%). Brown glassy solid. IR (KBr): 2149 (C≡C). ^{1}H NMR ($C_2D_2Cl_2$, 400 MHz, 100 °C): 8.03 (d, $J = 2$ Hz, 2H), 7.75 (t, $J = 2$ Hz, 1H), 7.50 (m, 8H), 5.08 (d, $J = 9$ Hz, 1H), 5.01 (s, 1H), 4.36 (d, $J = 9$ Hz, 1H), 2.91 (s, 3H), 1.23 (s, 42H). ^{13}C NMR ($CDCl_3$, 75 MHz): 145.54, 145.49, 145.39, 145.35, 145.26, 145.24, 145.18, 144.70, 144.57, 144.39, 144.36, 143.13, 143.00, 142.69, 142.60, 142.57, 142.25, 142.22, 142.13, 142.10, 142.04, 142.00, 141.94, 141.90, 141.68, 141.63, 140.20, 140.12, 139.69, 138.10, 137.11, 136.52, 135.95, 135.66, 134.92, 132.24, 132.17, 132.01, 131.48, 123.68, 122.65, 106.57, 93.07, 90.32, 90.24, 82.85, 69.98, 69.01, 40.13, 31.91, 29.70, 29.65, 29.35, 18.66, 11.30. Anal. Calcd for $C_{107}H_{59}NSi_2$, $2H_2O$: C 88.58, H 4.38, N 0.97; found: C 88.23, H 4.73, N 1.15. FAB MS: 1415.6 $[M + H]^+$ calculated for $C_{107}H_{60}NSi_2$ (1415.8).

4.7.2. Compound ***C_{60}-G2***

This compound was prepared from *N*-methylglycine (76 mg, 0.85 mmol), **6** (150 mg, 0.105 mmol), **C_{60}** (84 mg, 0.116 mmol) in toluene (95 mL) and column chromatography (SiO_2, hexane/CH_2Cl_2 8:2) yielded **C_{60}-G2** (120 mg, 52%). Brown glassy solid. IR (KBr): 2152 (C≡C). ^{1}H NMR ($C_2D_2Cl_2$, 400 MHz, 110 °C): 8.09 (d, $J = 2$ Hz, 2H), 7.79 (t, $J = 2$ Hz, 1H), 7.74 (d, $J = 2$ Hz, 4H), 7.72 (t, $J = 2$ Hz, 2H), 7.51 (m, 16H), 5.09 (d, $J = 10$ Hz, 1H), 5.04 (s, 1H), 4.38 (d, $J = 10$ Hz, 1H), 2.93 (s, 3H), 1.24 (s, 84H). ^{13}C NMR ($CDCl_3$, 75 MHz): 144.70, 144.56, 144.36, 143.13, 142.56, 142.27, 142.14, 142.01, 141.91, 141.67, 140.20, 138.30, 136.54, 135.98, 135.66, 134.29, 132.02, 131.47, 123.95, 123.79, 123.69, 122.53, 106.55, 93.14, 90.48, 89.47, 89.02, 69.01, 40.10, 29.70, 18.66. Anal. Calcd for $C_{161}H_{115}NSi_4$, CH_2Cl_2: C 86.06, H 5.22, N 0.62; found: C 86.39, H 5.55, N 0.86. FAB MS: 2176.4 $[M]^+$ calculated for $C_{161}H_{115}NSi_4$ (2176.0).

4.7.3. Compound ***C_{60}-Y1***

This compound was prepared from *N*-methylglycine (210 mg, 2.2 mmol), **8** (150 mg, 0.22 mmol), **C_{60}** (210 mg, 0.29 mmol) in toluene (230 mL) and column chromatography (SiO_2, hexane/toluene 4:1) yielded **C_{60}-Y1** (137 mg, 45%). Brown glassy solid. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.50–7.46 (m, 11H), 5.03 (d, $J = 10$ Hz, 1H), 4.95 (s, 1H), 4.31 (d, $J = 10$ Hz, 1H), 2.83 (s, 3H), 1.14 (s, 42H). ^{13}C NMR ($CDCl_3$, 50 MHz): 152.85, 147.27, 146.44, 146.24, 146.18, 146.12, 146.07, 145.93, 145.89, 145.82, 145.69, 145.54, 145.51, 145.45, 145.30, 145.22, 145.19, 144.66, 144.54, 144.36, 144.33, 143.10, 142.96, 142.65, 142.56, 142.18, 142.11, 142.06, 142.00, 141.95, 141.84, 141.65, 141.57, 140.15, 139.99, 139.64, 136.99, 136.43, 135.94, 135.66, 133.65, 132.98, 130.48, 129.71, 125.88, 106.54, 93.09, 69.05, 17.39, 17.20, 12.44, 10.07. Anal. Calcd for $C_{107}H_{59}NSi_2$: C 90.84, H 4.20, N 0.99; found: C 90.45, H 4.27, N 0.91. FAB MS: 1415.2 $[M]^+$ calculated for $C_{107}H_{59}NSi_2$ (1414.8).

4.7.4. Compound ***C_{60}-Y2***

This compound was prepared from *N*-methylglycine (63 mg, 0.7 mmol), **11** (100 mg, 0.07 mmol), **C_{60}** (66 mg, 0.09 mmol) in toluene (130 mL) and column chromatography (SiO_2, hexane/toluene 4:1) yielded **C_{60}-Y2** (60 mg, 43%). Brown glassy solid. ^{1}H NMR ($CDCl_3$, 200 MHz): 7.82–7.43 (m, 25H), 5.00 (d, $J = 10$ Hz, 1H), 4.96 (s, 1H), 4.30 (d, $J = 10$ Hz, 1H), 2.85 (s, 3H), 1.14 (s, 42H), 1.12 (s, 42H). ^{13}C NMR ($CDCl_3$, 50 MHz): 155.91, 153.69, 152.86, 152.46, 147.29, 146.42, 146.30, 146.28, 146.19, 146.17, 146.14, 146.09, 145.95, 145.92, 145.79, 145.70, 145.57, 145.52, 145.47, 145.37, 145.33, 145.24, 145.21, 145.17, 144.68, 144.55, 144.38, 144.33, 143.13, 142.97, 142.68, 142.58, 142.55, 142.53, 142.23, 142.20, 142.13, 142.09, 142.08, 142.01, 141.98, 141.88, 141.66, 141.59, 140.18, 139.68, 138.01, 137.04, 136.43, 135.98, 135.64, 135.04, 134.97, 132.09, 132.03, 131.94, 131.45, 131.36, 130.86, 126.12, 125.77, 125.54, 123.81, 123.71, 123.05, 122.70, 122.67,95.39, 94.13, 93.52, 93.41, 93.12, 93.02, 90.66, 89.84, 89.16, 89.13, 69.01, 40.05, 29.69, 18.66, 11.30. Anal. Calcd for $C_{161}H_{115}NSi_4$, CH_2Cl_2: C 86.06, H 5.22, N 0.62; found: C 86.28, H 5.42, N 0.56. FAB MS: 2176.8 $[M]^+$ calculated for $C_{161}H_{115}NSi_4$ (2176.0).

Acknowledgements

This work was supported by the CNRS. S. Z. and M. U. thank the French Ministry of Research, and A. G. the ADEME – Région Alsace for their fellowships.

References

[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. 124 (2002) 10875.
[3] (a) J.S. Moore, Z. Xu, Macromolecules 24 (1991) 5893; J.S. Moore, Z. Xu, J. Am. Chem. Soc. 116 (1994) 4537; (b) J.S. Moore, Z. Xu, Angew. Chem. Int. Ed. Engl. 32 (1993) 246.
[4] Z. Peng, Y. Pan, B. Xu, J. Zhang, J. Am. Chem. Soc. 122 (2000) 6619.
[5] J.-F. Nierengarten, S. Zhang, A. Gégout, M. Urbani, N. Armaroli, G. Marconi, Y. Rio, J. Org. Chem. 70 (2005) 7550.
[6] J.S. Moore, Acc. Chem. Res. 30 (1997) 402.
[7] (a) C. Devadoss, P. Bharathi, J.S. Moore, J. Am. Chem. Soc. 118 (1996) 9635; (b) Y. Pan, M. Lu, Z. Peng, J.S. Melinger, J. Org. Chem. 68 (2003) 6952.
[8] (a) N. Armaroli, F. Barigelletti, P. Ceroni, J.-F. Eckert, J.-F. Nicoud, J.-F. Nierengarten, Chem. Commun. (2000) 599; (b) G. Accorsi, N. Armaroli, J.-F. Eckert, J.-F. Nierengarten, Tetrahedron Lett. 43 (2002) 65; (c) J.-F. Nierengarten, N. Armaroli, G. Accorsi, Y. Rio, J.-F. Eckert, Chem. Eur. J. 9 (2003) 36; (d) N. Armaroli, G. Accorsi, J.N. Clifford, J.-F. Eckert, J.-F. Nierengarten, Chem. Asian J. 1 (2006) 564; (e) J.N. Clifford, A. Gégout, S. Zhang, R. Pereira de Freitas, M. Urbani, M. Holler, P. Ceroni, J.-F. Nierengarten, N. Armaroli, Eur. J. Org. Chem. (2007) 5899.
[9] (a) 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. 42 (2001) 3435; (b) J.L. Segura, R. Gomez, N. Martin, C.P. Luo, A. Swartz, D.M. Guldi, Chem. Commun. (2001) 707; (c) M. Schwell, N.K. Wachter, J.H. Rice, J.P. Galaup, S. Leach, R. Taylor, R.V. Bensasson, Chem. Phys. Lett. 339 (2001) 29; (d) L. Pérez, J.C. Garcia-Martinez, E. Diez-Barra, H. P.AtienzarGarcia, J. Rodriguez-Lopez, F. Langa, Chem. Eur. J. 12 (2006) 5149.
[10] (a) V. Balzani, S. Campagna, G. Denti, A. Juris, S. Serroni, M. Venturi, Acc. Chem. Res. 31 (1998) 26; (b) V. Balzani, P. Ceroni, A. Juris, M. Venturi, S. Campagna, F. Puntoriero, S. Serroni, Coord. Chem. Rev. 219 (2001) 545; (c) A. Adronov, J.M.J. Fréchet, Chem. Commun. (2000) 1701; (d) M. Fischer, F. Vögtle, Angew. Chem. Int. Ed. 38 (1999) 885.
[11] For reviews, see:(a) J.-F. Nierengarten, Sol. Energy Mater. Sol. Cells 83 (2004) 187; (b) J.-F. Nierengarten, New J. Chem. 28 (2004) 1177; (c) T.M. Figueira-Duarte, A. Gégout, J.-F. Nierengarten, Chem. Commun. (2007) 109.
[12] M. Prato, M. Maggini, Acc. Chem. Res. 31 (1998) 519.
[13] E.J. Corey, P.L. Fuchs, Tetrahedron Lett. 13 (1972) 3769.
[14] (a) T. Gu, J.-F. Nierengarten, Tetrahedron Lett. 42 (2001) 3175; (b) T. Gu, D. Tsamouras, C. Melzer, V. Krasnikov, J.-P. Gisselbrecht, M. Gross, G. Hadziioannou, J.-F. Nierengarten, ChemPhysChem. 3 (2002) 124; (c) J.-F. Nierengarten, T. Gu, G. Hadziioannou, D. Tsamouras, V. Krasnikov, Helv. Chim. Acta 87 (2004) 2948; (d) N. Armaroli, G. Accorsi, Y. Rio, P. Ceroni, V. Vicinelli, R. Welter, T. Gu, M. Saddik, M. Holler, J.-F. Nierengarten, New J. Chem. 28 (2004) 1627; (e) J.-F. Nierengarten, Pure Appl. Chem. 78 (2006) 847.
[15] J.S. Schumm, D.L. Pearson, J.M. Tour, Angew. Chem. Int. Ed. Engl. 33 (1994) 1360.
[16] U. Ziener, A. Godt, J. Org. Chem. 62 (1997) 6137.
[17] F. Ajamaa, T.M. Figueira Duarte, C. Bourgogne, M. Holler, P.W. Fowler, J.-F. Nierengarten, Eur. J. Org. Chem. (2005) 3766.