Tetrahedron 64 (2008) 11409–11419

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Synthesis of fullerene building blocks bearing alkyne or azide groups and their subsequent functionalization by the copper mediated Huisgen 1,3-dipolar cycloaddition

Rossimiriam Pereira de Freitas [a], Julien Iehl [b], Béatrice Delavaux-Nicot [c], Jean-François Nierengarten [b,*]

[a] Universidade Federal de Minas Gerais, Departamento de Química, Av. Antônio Carlos, 6627, 31270901 Belo Horizonte, MG, Brazil
[b] Laboratoire de Chimie des Matériaux Moléculaires, Université Louis Pasteur et CNRS (UMR 7509), Ecole Européenne de Chimie, Polymères et Matériaux (ECPM), 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
[c] Laboratoire de Chimie de Coordination du CNRS (UPR 8241), 205 route de Narbonne, 31077 Toulouse Cedex 4, France

ARTICLE INFO

Article history:
Received 31 July 2008
Received in revised form 5 September 2008
Accepted 12 September 2008
Available online 26 September 2008

Keywords:
Alkynes
Azides
Cycloadditions
Fullerene
Triazoles

ABSTRACT

C_{60} derivatives bearing either terminal alkyne or azide functional groups have been prepared and used as building blocks under the copper mediated Huisgen 1,3-dipolar cycloaddition conditions. In general, the reactivity of C_{60} toward azides does not significantly compete with the cycloaddition leading to the desired 1,2,3-triazole derivatives and good yields can be obtained when fullerene derivatives with reasonable solubility are used as starting materials. The electrochemical properties of the new fullerene derivatives have also been investigated by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV).

1. Introduction

Following the discovery of the macroscopic-scale [60]fullerene synthesis, the chemistry of this fascinating spherical molecule has been intensively investigated.[1] The chemical reactivity of C_{60} is now well established and a large number of fullerene derivatives have been prepared.[1] Owing to their facile multiple reducibility, optical non-linearity and/or efficient singlet oxygen photosensitization, fullerene-containing compounds have found applications in materials science[2] and biology.[3] Whereas most of the fullerene derivatives reported to date have been prepared by the direct functionalization of C_{60} in the final step, the use of fullerene building blocks in multi-step synthesis has been much scarcely considered. This is mainly associated with the chemical reactivity of the fullerene moiety. Effectively, C_{60} derivatives react readily with radicals, various nucleophiles, carbenes, and participate as reactive 2π components in a variety of cycloaddition reactions.[1] Thus the range of reactions that can be used for the further transformations of fullerene derivatives appears to be quite limited. Approaches which use the most common methanofullerene derivatives[4] as synthetic intermediates frequently involve reactions carried out under neutral or acid conditions. Examples are cleavage of protecting groups,[5] activation of carboxylic acid derivatives for subsequent esterification or preparation of amides,[6] construction of porphyrins,[7] and condensation reactions.[8] As a part of our research program on fullerene derivatives, we have recently evaluated the potential of click chemistry[9] to functionalize fullerene derivatives.[10,11] Such chemistry appears to be an attractive tool for fullerene chemistry as click reactions are modular, tolerant to a wide range of functional groups, and high yielding. The copper mediated Huisgen 1,3-dipolar cycloaddition of organic azides and alkynes[12] to give 1,2,3-triazoles is without any doubts the most useful member of this family of reactions. However, whereas this click reaction has proven to be powerful for a large variety of building blocks,[13] its compatibility with fullerene derivatives was not obvious, as organic azides may also undergo [3+2] cycloadditions to the [6,6] double bonds of fullerenes.[14] In this paper, we report a full account on our results concerning the use of the copper mediated Huisgen 1,3-dipolar cycloaddition starting from fullerene building blocks bearing either terminal alkyne or azide functional groups. In addition, the electrochemical properties of the resulting fullerene derivatives are described.

* Corresponding author.
E-mail addresses: rossipdf@yahoo.com.br (R. Pereira de Freitas), beatrice.delavaux-nicot@lcc-toulouse.fr (B. Delavaux-Nicot), nierengarten@chimie.u-strasbg.fr (J.-F. Nierengarten).

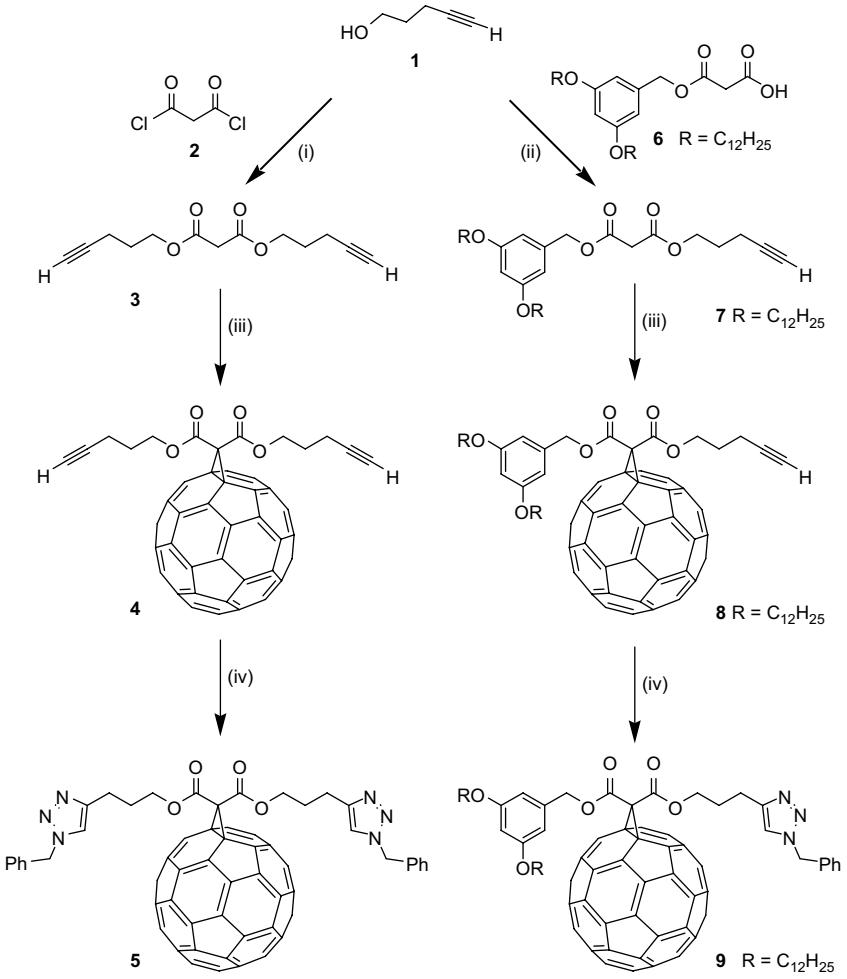
0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.09.047

2. Results and discussion

2.1. Synthesis

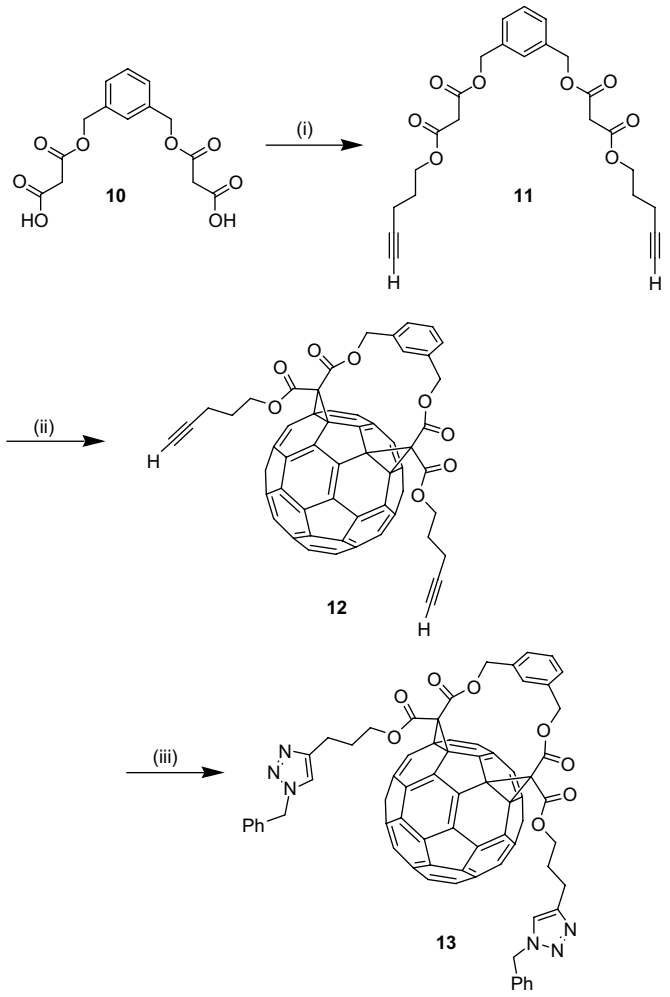
The first series of click reactions have been performed from fullerene derivatives functionalized with terminal alkyne groups. The preparation of alkyne **4** is depicted in Scheme 1. Reaction of commercial malonyl dichloride (**2**) with 4-pentyn-1-ol (**1**) in the presence of pyridine afforded malonate **3** in 77% yield. The reaction of compound **3** with C_{60}, iodine, and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) under Bingel conditions[15] gave methanofullerene **4** in 44% yield. Treatment of **4** (1 equiv) with benzyl azide (3 equiv), $CuSO_4 \cdot 5H_2O$ (0.1 equiv), and sodium ascorbate (0.3 equiv) in CH_2Cl_2/H_2O under vigorous stirring at room temperature for 96 h gave the cycloaddition product **5** in a moderate yield (48%). The solubility of compound **4** is quite low and all the starting material was not dissolved under the copper mediated Huisgen reaction conditions. Thus, the reaction was slow and side reactions, most probably cycloaddition of benzyl azides to the fullerene core, were observed. To solve this problem, we decided to prepare a more soluble methanofullerene-alkyne derivative bearing a 3,5-didodecyloxybenzyl group. *N*,*N*′-Dicyclohexylcarbodiimide (DCC)-mediated esterification of **1** with carboxylic acid **6** yielded malonate **7**. Subsequent treatment with C_{60}, iodine, and DBU afforded methanofullerene **8**. Owing to the good solubility of alkyne **8**, the reaction of this compound with benzyl azide in the presence of $CuSO_4 \cdot 5H_2O$ and sodium ascorbate in CH_2Cl_2/H_2O could be achieved under optimized concentration conditions. Compound **9** was thus obtained in a good yield (80%), thus showing that the reactivity of the fullerene moiety with organic azides plays only a minor role under copper mediated Huisgen 1,3-dipolar cycloaddition conditions.

To further decrease the reactivity of the C_{60} moiety toward the azide reagents in the click reactions, we have decided to prepare a fullerene bis-adduct bearing two terminal alkyne groups. It is well known that the reactivity of the fullerene unit is decreased by increasing the number of substituents on the carbon cage.[16] The synthesis of building block **12** is depicted in Scheme 2. Treatment of diacid **10** with 4-pentyn-1-ol (**1**) and DCC in the presence of 4-dimethylaminopyridine (DMAP) and 1-hydroxybenzotriazole (HOBt) gave bis-malonate **11** in 58% yield. Fullerene derivative **12** was then prepared by taking advantage of the versatile regioselective reaction developed by Diederich et al.,[17] which led to macrocyclic bis-adducts of C_{60} by a cyclization reaction at the carbon sphere with bis-malonate derivatives in a double Bingel[15] cyclopropanation. Reaction of **11** with C_{60}, I_2, and DBU in toluene at room temperature afforded the desired cyclization product **12** in 44% yield. The relative position of the two cyclopropane rings in **12** on the C_{60} core has been determined based on the molecular symmetry (C_s) deduced from the ^1H and ^{13}C NMR spectra. It is also well established that the 1,3-phenylenebis(methylene)-tethered bis-malonates produce regioselectively the C_s symmetrical cis-2 addition pattern at C_{60}.[17,18] Reaction of **12** with benzyl azide under the conditions optimized for the preparation of compound **9** gave bis-



Scheme 1. Reagents and conditions: (i) CH_2Cl_2, pyridine, rt (77%); (ii) DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt (59%); (iii) C_{60}, DBU, I_2, PhMe, rt (**4**: 44%, **8**: 31%); (iv) benzyl azide, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (**5**: 48%, **9**: 80%).

1,2,3-triazole **13** in 70% yield. When compared to the preparation of compound **5** from methanofullerene **4**, the increased yield can be explained by both the higher solubility of the starting terminal alkyne and the decreased reactivity of the bis-substituted fullerene group.



Scheme 2. Reagents and conditions: (i) **1**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt (58%); (ii) C_{60}, DBU, I_2, PhMe, rt (44%); (iii) benzyl azide, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (70%).

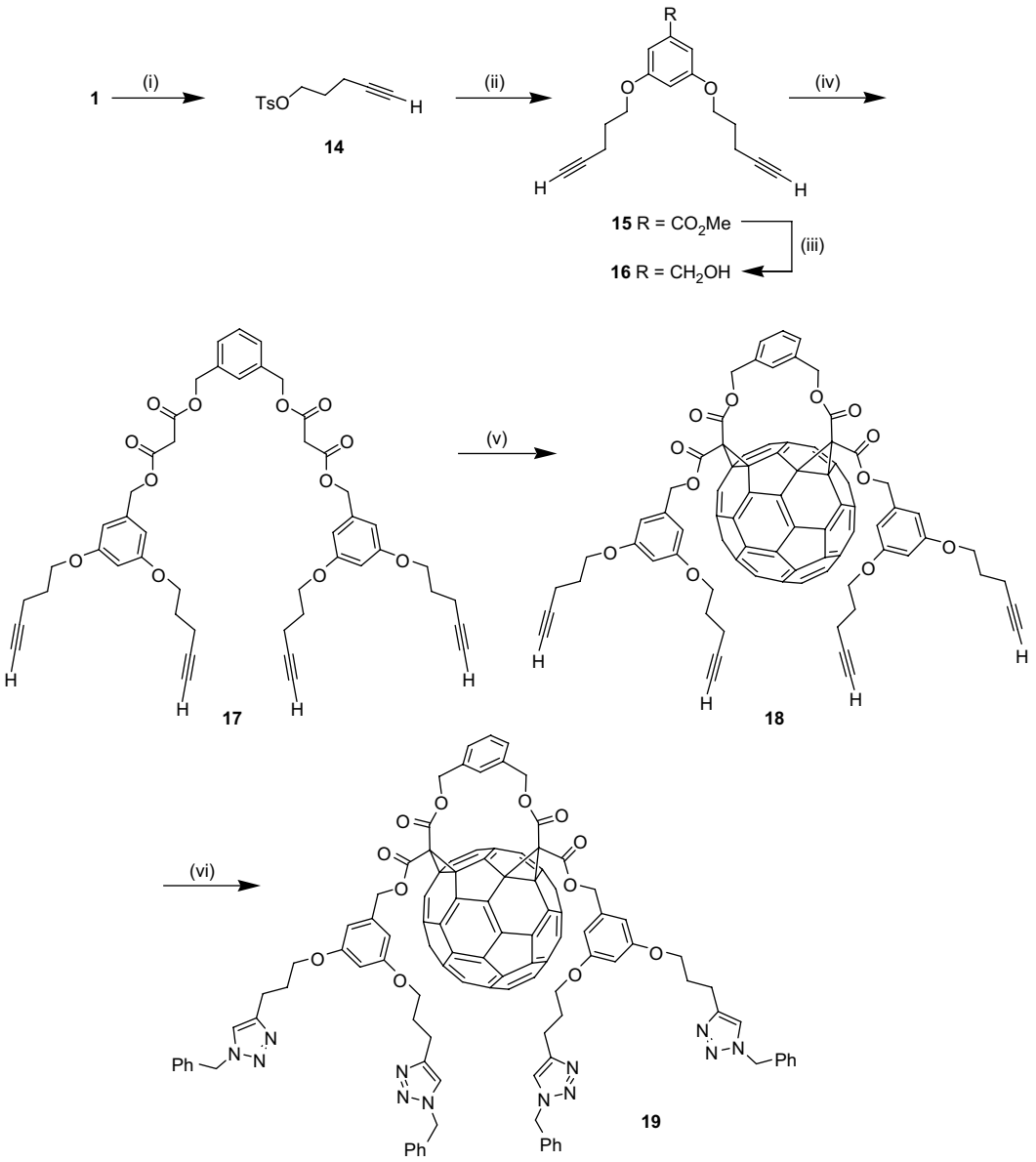
These results prompted us to further investigate the synthesis of a fullerene bis-adduct bearing four terminal alkyne groups allowing the simultaneous grafting of four azide derivatives under click conditions. The synthesis of fullerene derivative **18** is depicted in Scheme 3. Conversion of 4-pentyn-1-ol (**1**) to the corresponding tosylate was easily carried out under classic conditions and gave compound **14** in 73% yield. Alkylation of commercial methyl-3,5-dihydroxybenzoate with **14** afforded intermediate **15** in 81% yield. Subsequent treatment of **15** with LAH gave benzylic alcohol **16** in 83% yield. The reaction of diacid **10** with alcohol **16** and DCC in the presence of DMAP and HOBt gave bis-malonate **17** in 74% yield. A double Bingel[15] cyclopropanation was used to prepare fullerene bis-adduct derivative **18**. Reaction of **17** with C_{60}, I_2, and DBU in toluene at room temperature afforded the desired cyclization product **18** in 39% yield. The copper mediated Huisgen 1,3-dipolar cycloaddition reaction of **18** with benzyl azide gave tetra-1,2,3-triazole **19** in a moderate yield (39%).

In a second series of click reactions, we have evaluated the use of fullerene building blocks functionalized with azide groups. To this end, the synthesis of methanofullerene derivatives substituted with one or two azide groups was attempted. Unfortunately, these compounds were found to be very unstable in the solid state although reasonably stable in solution. Most probably, intermolecular cycloaddition reactions between the C_{60} and the azide groups led to complex mixtures of polymeric compounds. Actually, only fullerene bis-adducts were sufficiently stable to be used as synthetic intermediates in click reactions. This observation confirms the decreased reactivity of the fullerene moiety by increasing the number of substituents on the carbon cage. The preparation of the building block **23** is depicted in Scheme 4. Reaction of bis-malonic acid **10** with alcohol **20** under esterification conditions (DCC, DMAP, HOBt) yielded bis-malonate **21**. Subsequent treatment with sodium azide in DMF at room temperature gave **22** in 76% yield. Bis-adduct **23** was then obtained in 16% yield by reaction of **22** with C_{60}, I_2, and DBU in toluene at room temperature. Upon purification, diazide **23** should be used for the click reactions within the next 4 h to obtain good yields. Reaction of **23** with phenylacetylene under optimized conditions afforded bis-1,2,3-triazole **24** in 78% yield. The structure of compound **24** was confirmed by its ^1H and ^{13}C NMR spectrum as well as by mass spectrometry. Inspection of the ^1H NMR spectra clearly indicates the disappearance of the CH_2-azide signal at δ 3.41 ppm. Importantly, the ^1H NMR spectrum of **24** shows the typical singlet of the 1,2,3-triazole unit at δ 7.75 ppm as well as the signal corresponding to the CH_2-triazole protons at δ 4.42 ppm. The click reaction conditions were also used to produce derivative **25** from terminal alkyne **8** and bis-azide **23**. The structure of **25** was confirmed by MALDI-TOF mass spectrometry showing the expected molecular ion peak at m/z 3889 ($[MH]^+$, calcd for $C_{278}H_{145}N_6O_{20}$: 3889.24).

Finally, it was also possible to prepare a bis-methanofullerene bearing four azide groups that was stable enough to be used in click reactions. The synthesis of compound **30** is shown in Scheme 5. Tosylation of azide-alcohol **26** followed by alkylation of 3,5-dihydroxybenzyl alcohol gave compound **28** in 40% yield. Bis-malonate **29** was obtained in 48% yield by reaction between diacid **10** and alcohol **28** under esterification conditions (DCC, DMAP, HOBt). The preparation of fullerene bis-adduct **30** from bis-malonate **29** under Diederich conditions[17] was then achieved in 10% yield. Compound **31** resulting from four simultaneous click reactions between tetra-azide **30** and terminal alkyne **8** was then obtained in 34% yield. Owing to the presence of two pendant alkyl chains per peripheral fullerene moiety, compound **31** is well soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF or toluene, and spectroscopic characterization was easily achieved. The ^1H NMR spectrum of **31** shows the typical pattern of the central 1,3-phenylenebis(methylene)-bridged fullerene bis-adduct with the expected additional signals arising from the four equivalent substituted methanofullerenes. The integration ratios are also consistent with the proposed molecular structure. Finally, the expected molecular ion peak is observed at m/z 6994.5 ($[MH]^+$, calcd for $C_{496}H_{291}N_{12}O_{36}$: 6994.83) in the MALDI-TOF mass spectrum of **31**.

2.2. Electrochemistry

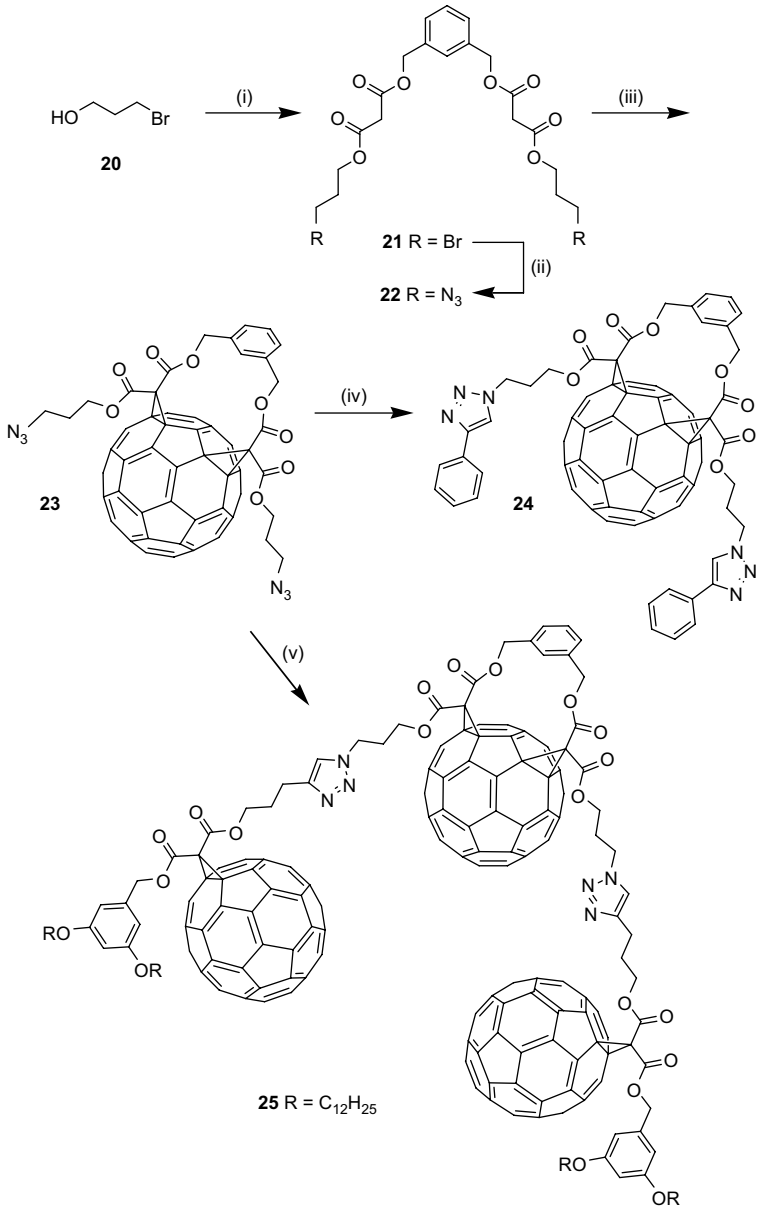
The electrochemical properties of compounds **8**, **9**, **12**, **13**, **18**, **19**, and **24** were determined by cyclic voltammetry (CV) and Osteryoung Square Wave Voltammetry (OSWV). All the experiments were performed at room temperature in CH_2Cl_2 solutions containing tetra-*n*-butylammonium tetrafluoroborate (0.1 M) as supporting electrolyte and ferrocene (Fc) as internal reference, with a Pt wire as the working electrode and a saturated calomel electrode (SCE) as a reference. Potential data for all of the compounds are collected in Table 1. As typical examples, the cyclic voltammograms obtained from **8** and **13** are shown in Figure 1.



Scheme 3. Reagents and conditions: (i) TsCl, pyridine, CH_2Cl_2, 0 °C to rt (73%); (ii) methyl-3,5-dihydroxybenzoate, K_2CO_3, LiBr, DMF, 80 °C (81%); (iii) $LiAlH_4$, THF, 0 °C (83%); (iv) **10**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt (74%); (v) C_{60}, DBU, I_2, PhMe, rt (39%); (vi) benzyl azide, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (39%).

In the anodic region, all the studied compounds present at least one irreversible peak at ca. +1.1–1.4 V versus Fc/Fc^+, which can be likely attributed to the oxidation of the dialkyloxyphenyl and/or dialkylphenyl units.[19] In the cathodic region, fullerene derivatives **8**, **9**, **12**, **13**, **18**, **19**, and **24** essentially retain the electrochemical pattern of the parent fullerene but the reduction potentials of all of these species are shifted to more negative values when compared to those of pristine C_{60}. This is the classical behavior observed for most fullerene derivatives, the cyclic voltammograms of which are typically characterized by small shifts to more negative potentials as the saturation of a double bond on the C_{60} surfaces causes a partial loss of 'conjugation'.[20] There are, however, no significant differences between the reduction potentials of mono-adducts **8** and **9** when compared to those of the cis-2 bis-adducts **12**, **13**, **18**, **19**, and **24**. Whereas the first reduction observed at ca. −1.05 to −1.10 V versus Fc/Fc^+ is always reversible, the second is irreversible at low scan rates (0.1 V s^{-1}) but becomes reversible at scan rates higher than 2 V s^{-1} in accordance with already reported observations on other C_{60} derivatives.[21] The third wave gradually disappears when the second one becomes reversible, so that it probably implies reduction of the product formed after the second reduction. It is worth mentioning that this effect is relatively limited for mono-adducts **8** and **9** but becomes important for bis-adducts **12**, **13**, **18**, **19**, and **24** (Fig. 2). While CV experiments were unable to detect clearly the next reduction waves, OSWV revealed such processes easily (Fig. 3). The reduction observed at ca. −1.88 to −1.92 V versus Fc/Fc^+ corresponds to the redox couple C_{60}^{3-}/C_{60}^{2-} and the wave at ca. –2.06 to −2.11 V versus Fc/Fc^+ to the reduction of an electrogenerated species.[21] Finally, the reduction seen at ca. −2.28 to −2.45 V versus Fc/Fc^+ is ascribed to the C_{60}^{4-}/C_{60}^{3-} redox couple.

The electrochemical properties of compounds **25** and **31** were also investigated. The electrochemical behavior of **25** and **31** in both CV and OSWV (Figs. 1 and 3) appears to be similar to that of compounds **8**, **9**, **12**, **13**, **18**, **19**, and **24**. The reduction potentials are also quite similar (Table 1). This seems to indicate that the different fullerene units in **25** and **31** behave as independent redox centers. The electrochemical behavior of the two kinds of fullerene subunits



Scheme 4. Reagents and conditions: (i) **10**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt (46%); (ii) NaN_3, DMF, rt (76%); (iii) C_{60}, DBU, I_2, PhMe, rt (16%); (iv) phenylacetylene, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (78%); (v) **8**, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (50%).

present in both **25** and **31**, i.e., mono- and bis-adducts, is similar and it was not possible to observe separate waves for both of them.

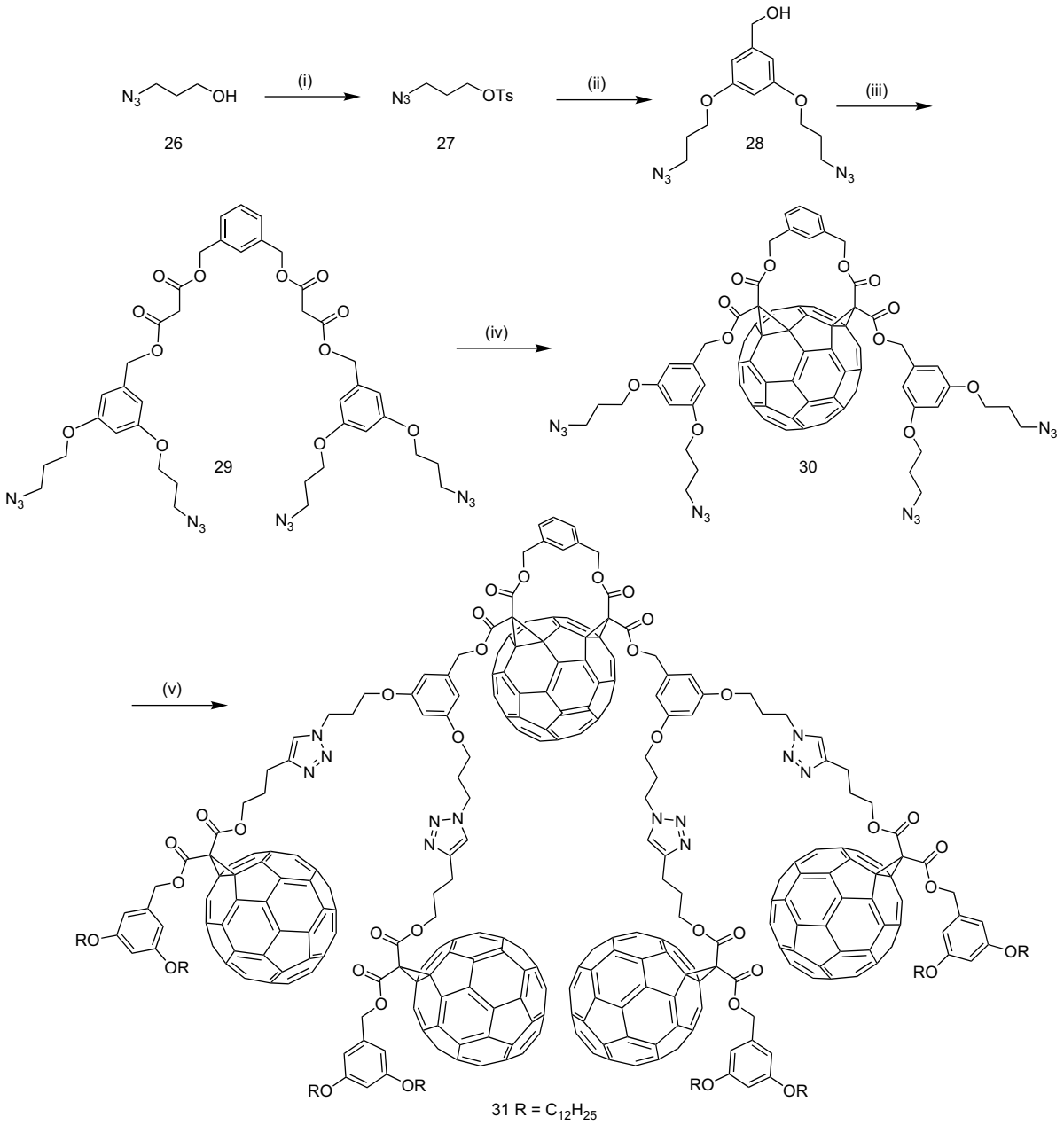
3. Conclusions

To sum up, we have shown that click chemistry is an interesting tool for the functionalization of fullerene building blocks. The chemical transformation of fullerene derivatives bearing azides and alkynes under the copper mediated Huisgen 1,3-dipolar cycloaddition conditions was demonstrated. Whereas the preparation of fullerene azide derivatives is difficult due to their fast decomposition, fullerene alkyne building blocks are easy to produce. In general, the reactivity of C_{60} toward azides is not significantly competing with the cycloaddition leading to the desired 1,2,3-triazole derivatives and good yields can be obtained when fullerene derivatives with reasonable solubility are used as starting materials. In particular, bis-adduct derivatives bearing alkyne groups appear to be the most promising building blocks for the synthesis of more complex fullerene derivatives. Work in this direction is now under investigation in our laboratory.

4. Experimental

4.1. General

Reagents and solvents were purchased as reagent grade and used without further purification. THF was distilled over 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



Scheme 5. Reagents and conditions: (i) TsCl, Et_3N, CH_2Cl_2, 0 °C to rt (75%); (ii) 3,5-dihydroxybenzyl alcohol, K_2CO_3, LiBr, DMF, 80 °C (40%); (iii) **10**, DCC, DMAP, HOBt, CH_2Cl_2, 0 °C to rt (48%); (iv) C_{60}, DBU, I_2, PhMe, rt (10%); (v) **8**, $CuSO_4 \cdot 5H_2O$, sodium ascorbate, CH_2Cl_2/H_2O, rt (34%).

with solvent peaks as reference. Mass measurement was carried out on a ZA HF instrument (FAB) with 4-nitrobenzyl alcohol as matrix or on a Bruker BIFLEX™ matrix-assisted laser desorption time-of-flight mass spectrometer (MALDI-TOF) with 1,8,9-trihydroxyanthracene (dithranol) as matrix. Elemental analysis were performed by the analytical service at the Laboratoire de Chimie de Coordination (Toulouse, France).

4.2. Electrochemistry

The electrochemical measurements were carried out with a potentiostat Autolab PGSTAT100. Experiments were performed at room temperature in a homemade airtight three-electrode cell connected to a vacuum/argon line. The reference electrode consisted of a saturated calomel electrode (SCE) separated from the solution by a bridge compartment. The counter electrode was a platinum wire of ca. 1 cm^2 apparent surface. The working electrode was a Pt microdisk (0.5 mm diameter). The supporting electrolyte *n*-Bu_4NBF_4 (Fluka, 99% electrochemical grade) was used as received and simply degassed under argon. Dichloromethane was freshly distilled over CaH_2 prior to use. The solutions used during the electrochemical studies were typically 10^{-3} M in compound and 0.1 M in supporting electrolyte. Before each measurement, the solutions were degassed by bubbling Ar and the working electrode was polished with a polishing machine (Presi P230). Under these experimental conditions, Fc/Fc^+ is observed at $+0.54 \pm 0.01$ V versus SCE.

4.2.1. Compound ***3***

Malonyl dichloride (350 mg, 2.48 mmol) was added to a stirred solution of 4-pentyn-1-ol (420 mg, 4.96 mmol) and pyridine (0.4 mL, 4.96 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After 1 h, the mixture was allowed to warm up to room temperature (within 1 h) and stirred for 24 h. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2,

Table 1
Electrochemical data of **8**, **9**, **12**, **13**, **18**, **19**, **24**, **25**, and **31** determined by OSWV on a Pt working electrode in CH_2Cl_2+0.1 M *n*-Bu_4NBF_4 at room temperature in the presence of ferrocene used as internal reference[a,b]

	Oxidation	Reduction					
	E_1	E_1	E_2	E_3	E_4	E_5	E_6
8	+1.11	−1.07	−1.46	−1.68[c]	−1.91	−2.11[c]	−2.33
9	+1.10	−1.05	−1.43	−1.67[c]	−1.90	−2.10[c]	−2.32
12	+1.18	−1.08	−1.39	−1.68[c]	−1.88	−2.07[c]	−2.28
13	+1.29	−1.07	−1.39	−1.68[c]	−1.89	−2.08[c]	−2.38
18	+1.12	−1.10	−1.40	−1.70[c]	−1.92	−2.09[c]	−2.45
19	+1.38	−1.06	−1.38	−1.68[c]	−1.90	−2.10[c]	−2.42
24	+1.29	−1.05	−1.37	−1.66[c]	−1.88	−2.06[c]	−2.40
25	+1.27	−1.05	−1.40	−1.68[c]	−1.90	−2.09[c]	−2.28
31	+1.16	−1.10	−1.39	−1.58[c]	−1.90	−2.09[c]	—

[a] OSWVs were obtained using a sweep width of 20 mV, a frequency of 10 Hz, and a step potential of 5 mV.
[b] Values in V versus Fc/Fc^+.
[c] Waves corresponding to an electrogenerated species obtained after the second reduction step.

CH_2Cl_2) gave **3** (450 mg, 77%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.80 (m, 4H), 1.91 (t, J=3 Hz, 2H), 2.20 (m, 4H), 3.30 (s, 2H), 4.17 (t, J=6 Hz, 4H).

*4.2.2. Compound **4***

DBU (0.25 mL, 1.72 mmol) was added to a stirred solution of C_{60} (500 mg, 0.69 mmol), I_2 (260 mg, 1.03 mmol), and **3** (163 mg, 0.69 mmol) in toluene (500 mL) at room temperature. The resulting solution was stirred for 6 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, toluene) gave **4** (290 mg, 44%) as a dark-red glassy product. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.07 (m, 6H), 2.42 (m, 4H), 4.62 (t, J=6 Hz, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.2, 27.3, 52.0, 65.8, 67.6, 69.7, 71.5, 82.4, 139.0, 141.0, 141.9, 142.2, 143.0, 143.0, 143.1, 143.9, 144.6, 144.7, 144.9, 145.1, 145.2, 145.3, 163.5. Anal. Calcd for $C_{73}H_{14}O_4 \cdot 2/3CH_2Cl_2$: C, 87.93; H, 1.53. Found: C, 87.79; H, 1.48. FABMS: 955 ($[M]^+$, calcd for $C_{73}H_{14}O_4$: 954.91).

*4.2.3. Compound **5***

To a mixture of **4** (92 mg, 0.096 mmol) and benzyl azide (39 mg, 0.293 mmol) in CH_2Cl_2 (2 mL) and H_2O (2 mL) were added $CuSO_4 \cdot 5H_2O$ (2 mg, 0.012 mmol) and sodium ascorbate (6 mg, 0.030 mmol). The reaction mixture was stirred for 96 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, toluene/AcOEt 7:3) gave **5** (75 mg, 48%) as a dark-red glassy product. IR (neat): 1738 (C=O). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.22 (m, 4H), 2.85 (t, J=7 Hz, 4H), 4.52 (t, J=6 Hz, 4H), 5.48 (s, 4H), 7.29 (m, 12H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ=22.1, 28.1, 50.9, 54.0, 66.5, 67.2, 71.5, 121.0, 128.0, 128.7, 129.1, 134.8, 138.9, 140.9, 141.8, 142.2, 142.9, 143.0, 143.1, 143.9, 144.5, 144.6, 144.7, 144.9, 145.1, 145.2, 145.2, 145.3, 146.8, 163.5. Anal. Calcd for $C_{87}H_{28}N_6O_4 \cdot CH_2Cl_2$: C, 80.92; H, 2.32; N, 6.43. Found: C, 81.04; H, 2.94; N, 6.50. FABMS: 1221 ($[M]^+$, calcd for $C_{87}H_{28}N_6O_4$: 1221.22).

*4.2.4. Compound **7***

DCC (1.10 g, 5.34 mmol), HOBt (cat), and DMAP (75 mg, 0.71 mmol) were added to a solution of 4-pentyn-1-ol (86 mg, 1.96 mmol) and **6** (1.10 g, 1.78 mmol), in CH_2Cl_2 (50 mL) at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, and was then stirred for 22 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexanes 1:1) gave **7** (697 mg, 59%) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J=7 Hz, 6H), 1.26–1.46 (m, 36H), 1.71–1.90 (m, 6H), 1.96 (t, J=2 Hz, 1H), 2.26 (m, 2H), 3.43 (s, 2H), 3.92 (t, J=6 Hz, 4H), 4.26 (t, J=6 Hz, 2H), 5.10 (s, 2H), 6.41 (t, J=2 Hz, 1H), 6.46 (d, J=2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 15.0, 22.7, 26.0, 27.3, 29.2, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 41.5, 64.0, 67.2, 68.0, 69.1, 82.7, 101.1, 106.5, 137.2, 160.5, 166.2, 166.3.

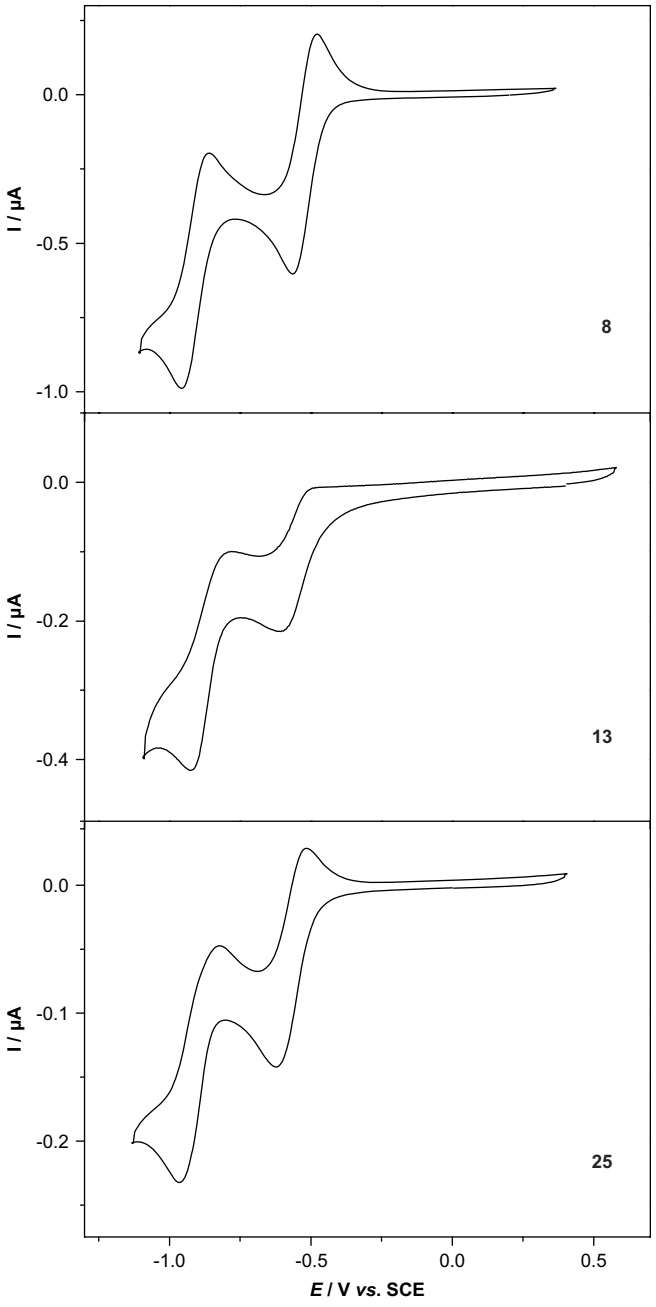


Figure 1. Cyclic voltammograms showing the two first reductions of **8**, **13**, and **25** on a Pt electrode at v=0.1 V s^{-1} in CH_2Cl_2+0.1 M *n*-Bu_4NBF_4.

*4.2.5. Compound **8***

DBU (0.19 mL, 1.27 mmol) was added to a stirred solution of C_{60} (458 mg, 0.64 mmol), I_2 (193 mg, 0.76 mmol), and **7** (400 mg, 0.64 mmol) in toluene (450 mL) at room temperature. The resulting solution was stirred for 6 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, hexanes/CH_2Cl_2 80:20) gave **8** (529 mg, 31%) as a dark-red solid. IR (neat): ν 3309 (≡C–H), 1745 (C=O). ^1H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J=7 Hz, 6H), 1.20–1.41 (m, 36H), 1.75 (m, 4H), 2.02 (m, 3H), 2.36 (m, 2H), 3.90 (t, J=7 Hz, 4H), 4.58 (t, J=7 Hz, 2H), 5.43 (s, 2H), 6.42 (t, J=2 Hz, 1H), 6.60 (d, J=2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 15.1, 22.7, 26.1, 27.2, 29.2, 29.3, 29.4, 29.6, 29.6, 29.7, 31.9, 51.9,

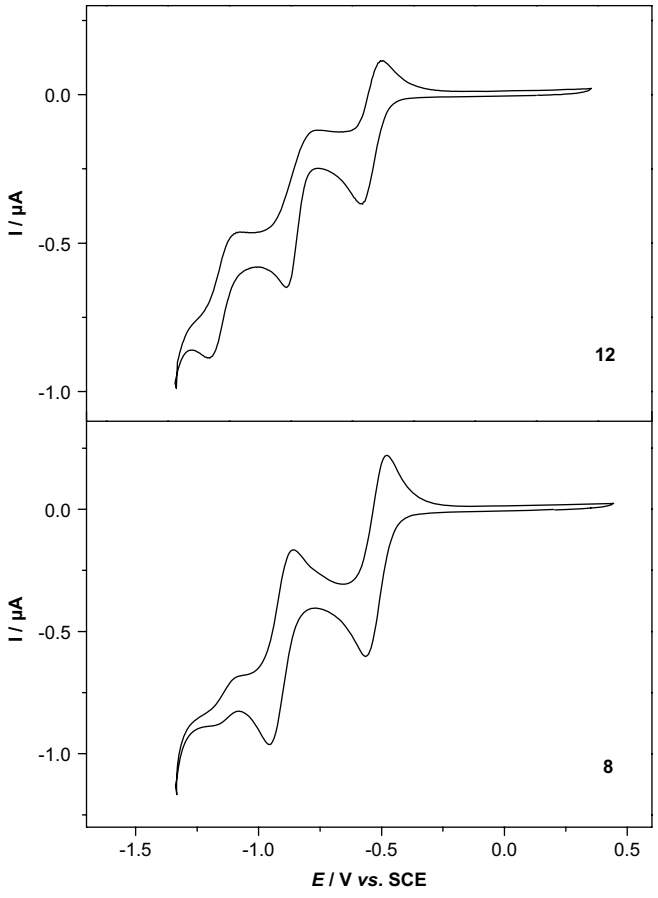


Figure 2. Cyclic voltammograms showing the three first reductions of **8** and **12** on a Pt electrode at v=0.1 V s^{-1} in CH_2Cl_2+0.1 M n-Bu_4NBF_4.

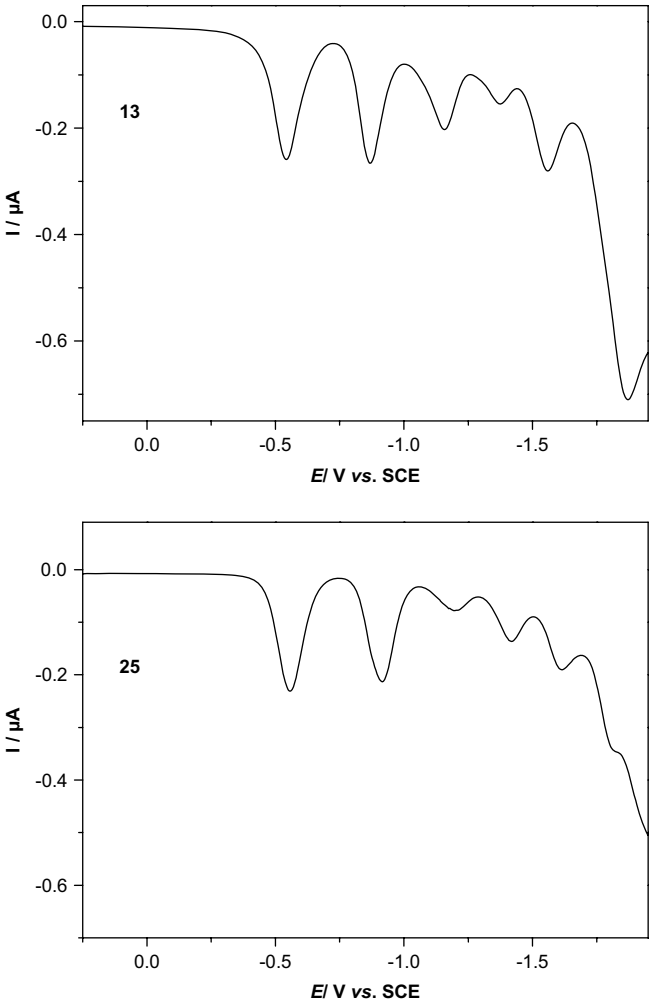


Figure 3. OSWVs (cathodic scan) of compounds **13** and **25** on a Pt electrode in CH_2Cl_2+0.1 M n-Bu_4NBF_4 at room temperature.

65.7, 68.1, 68.9, 69.6, 71.4, 82.5, 101.7, 107.2, 136.4, 138.7, 139.3, 140.8, 140.9, 141.8, 141.9, 142.1, 142.2, 142.8, 142.9, 143.0, 143.7, 143.8, 144.4, 144.5, 144.6, 144.8, 144.9, 145.0, 145.0, 145.1, 145.2, 160.5, 163.3, 163.4. Anal. Calcd for $C_{99}H_{62}O_6 \cdot 1/2\ CHCl_3$: C, 84.92; H, 4.48. Found: C, 85.17; H, 4.66.

*4.2.6. Compound **9***

To a mixture of **8** (114 mg, 0.084 mmol) and benzyl azide (22 mg, 0.165 mmol) in CH_2Cl_2 (2 mL) and H_2O (2 mL) were added $CuSO_4 \cdot 5H_2O$ (1 mg, 0.006 mmol) and sodium ascorbate (4 mg, 0.02 mmol). The reaction mixture was stirred for 4 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, hexane/CH_2Cl_2/MeOH 49:49:2) gave **9** (99 mg, 80%) as a dark-red glassy product. IR (neat): 1735 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.88 (t, J=7 Hz, 6H), 1.22–1.45 (m, 36H), 1.73 (m, 4H), 2.20 (m, 2H), 2.84 (t, J=7 Hz, 2H), 3.87 (t, J=7 Hz, 4H), 4.50 (t, J=6 Hz, 2H), 5.42 (s, 2H), 5.49 (s, 2H), 6.38 (t, J=2 Hz, 1H), 6.58 (d, J=2 Hz, 2H), 7.37 (m, 6H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 22.1, 22.7, 26.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.7, 31.9, 51.9, 66.5, 68.2, 68.9, 71.4, 101.6, 107.2, 121.0, 128.0, 128.7, 129.1, 136.8, 138.7, 139.2, 140.8, 141.8, 142.2, 143.0, 143.8, 144.4, 144.5, 144.6, 144.8, 145.0, 145.1, 145.2, 45.3, 160.5, 163.3, 163.3. Anal. Calcd for $C_{106}H_{69}N_3O_6 \cdot 1.3\ CH_2Cl_2$: C, 81.05; H, 4.64; N, 2.74. Found: C, 80.82; H, 4.88; N, 3.00. FABMS: 1481 ($[M]^+$, calcd for $C_{106}H_{69}N_3O_6$: 1480.73).

*4.2.7. Compound **11***

DCC (627 mg, 3.07 mmol), HOBt (cat), and DMAP (75 mg, 0.61 mmol) were added to a solution of 4-pentyn-1-ol (270 mg, 3.22 mmol) and **10** (476 mg, 1.54 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, and was then stirred for 60 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/AcOEt 1:1) gave **11** (390 mg, 58%) as a yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.85 (m, 4H), 1.98 (t, J=3 Hz, 2H), 2.24 (m, 4H), 3.44 (s, 4H), 4.25 (t, J=6 Hz, 4H), 5.19 (s, 4H), 7.31–7.39 (m, 4H).

*4.2.8. Compound **12***

DBU (0.30 mL, 1.91 mmol) was added to a stirred solution of C_{60} (300 mg, 0.42 mmol), I_2 (264 mg, 1.04 mmol), and **11** (183 mg, 0.42 mmol) in toluene (600 mL) at room temperature. The resulting solution was stirred for 6 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, hexane/CH_2Cl_2 50:50) gave **12** (206 mg, 44%) as a dark-red solid. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.94–2.00 (m, 6H), 2.32 (m, 4H), 4.39–4.57 (m, 4H), 5.2 (d, J=12 Hz, 2H), 5.9 (d, J=12 Hz, 2H), 7.30–7.54 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 27.2, 49.2, 65.5, 67.0, 67.5, 69.6, 70.6, 82.4, 123.9, 126.8, 128.7, 134.6, 135.9, 136.3, 136.6, 137.8, 140.0, 141.1, 141.4, 142.4, 142.9, 143.4, 143.6, 143.8, 144.1, 144.2, 144.3, 144.4, 144.7, 145.1, 145.3, 145.4, 145.7, 145.8, 145.8, 146.0, 146.1, 147.4, 147.5, 147.6, 148.7, 162.8, 162.9. Anal. Calcd for $C_{84}H_{22}O_8 \cdot CH_2Cl_2$: C, 82.07; H, 1.94. Found: C, 81.82; H, 2.19. FABMS: 1159 ($[M]^+$, calcd for $C_{84}H_{22}O_8$: 1159.09).

*4.2.9. Compound **13***

To a mixture of **12** (75 mg, 0.06 mmol) and benzyl azide (26 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) and H_2O (2 mL) were added

$CuSO_4 \cdot 5H_2O$ (1 mg, 0.006 mmol) and sodium ascorbate (4 mg, 0.02 mmol). The reaction mixture was stirred for 60 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, toluene/AcOEt 7:3) gave **13** (64 mg, 70%) as a dark-red glassy product. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.10 (m, 4H), 2.80 (t, J=7 Hz, 4H), 4.38 (m, 4H), 5.20 (d, J=12 Hz, 2H), 5.47 (s, 4H), 5.80 (d, J=12 Hz, 2H), 7.15 (m, 15H), 7.30 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 21.9, 28.1, 49.3, 54.0, 66.2, 67.0, 67.5, 70.7, 120.9, 123.9, 126.8, 128.0, 128.7, 129.1, 130.0, 134.8, 135.8, 136.2, 136.6, 140.0, 140.9, 141.3, 142.3, 143.0, 143.3, 143.6, 143.8, 144.0, 144.2, 144.3, 144.4, 144.7, 145.0, 145.2, 145.3, 145.4, 145.7, 145.8, 145.8, 146.1, 146.8, 147.4, 147.6, 148.6, 162.8, 162.9. Anal. Calcd for $C_{98}H_{36}N_6O_8 \cdot 4.8CH_2Cl_2$: C, 67.36; H, 2.51; N, 4.50. Found: C, 67.43; H, 2.93; N, 4.52. MALDI-TOF: 1426 ($[MH]^+$, calcd for $C_{98}H_{37}N_6O_8$: 1426.41).

4.2.10. Compound **14**

To a solution of 4-pentyn-1-ol (10 g, 0.119 mol) and pyridine (9.62 mL, 0.119 mol) in CH_2Cl_2 (100 mL) at 0 °C were added tosyl chloride (25 g, 0.131 mol) and DMAP (2.9 g, 0.238 mol). After 1 h, the mixture was allowed to warm slowly to room temperature, then stirred for 18 h, filtered, and evaporated. The organic layer was diluted with CH_2Cl_2, washed with water, then brine, dried with $MgSO_4$, and concentrated in vacuo. The crude product was purified by column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) to give **14** (20.73 g, 73%) as a colorless oil. IR (neat): ν 3289 (≡C–H). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.85 (m, 2H), 1.88 (t, J=3 Hz, 1H), 2.26 (m, 2H), 2.44 (s, 3H), 4.14 (t, J=6 Hz, 2H), 7.34 (d, J=8 Hz, 2H), 7.79 (d, J=8 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.9, 21.6, 27.7, 68.7, 69.4, 82.1, 127.9, 129.8, 132.9, 144.8. Anal. Calcd for $C_{12}H_{14}O_3S$: C, 60.48; H, 5.92. Found: C, 60.51; H, 5.58.

4.2.11. Compound **15**

A mixture of methyl-3,5-dihydroxybenzoate (0.88 g, 5.24 mmol), **14** (2.49 g, 10.47 mmol), K_2CO_3 (3.98 g, 28.82 mmol), and LiBr (0.682 g, 7.86 mmol) in dry DMF (10 mL) was stirred at 80 °C for 60 h. The mixture was cooled to room temperature, filtered, and evaporated. The crude product was then purified by column chromatography (SiO_2, CH_2Cl_2/hexane 70:30) to give **15** (1.28 g, 81%) as a white solid. IR (neat): ν 3289 (≡C–H), 1713 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97 (t, J=3 Hz, 2H), 2.00 (m, 4H), 2.40 (m, 4H), 3.89 (s, 3H), 4.08 (t, J=6 Hz, 4H), 6.65 (t, J=2 Hz, 1H), 7.18 (d, J=2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 28.0, 52.2, 66.4, 68.9, 83.3, 106.6, 107.8, 131.9, 159.9, 166.8. Anal. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71. Found: C, 71.84; H, 6.58.

4.2.12. Compound **16**

A 1 M LAH solution in THF (3 mL, 3 mmol) was added dropwise to a stirred solution of **15** (1.28 g, 4.26 mmol) in THF (20 mL) at 0 °C. The resulting mixture was stirred for 6 h at 0 °C, then MeOH was carefully added. The organic layer (diluted with CH_2Cl_2) was washed with water, then brine, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.5:0.5) gave **16** (0.967 g, 83%) as a yellow oil. IR (neat): ν 3400 (O–H), 3290 (≡C–H). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97 (t, J=3 Hz, 2H), 1.98 (m, 4H), 2.39 (m, 4H), 4.03 (t, J=6 Hz, 4H), 4.59 (s, 2H), 6.38 (t, J=2 Hz, 1H), 6.50 (d, J=2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 28.1, 65.2, 66.1, 68.9, 83.4, 100.5, 105.2, 143.3, 160.2. Anal. Calcd for $C_{17}H_{20}O_3$: C, 74.97; H, 7.40. Found: C, 74.54; H, 7.11.

4.2.13. Compound **17**

DCC (1.01 g, 4.97 mmol), HOBt (cat), and DMAP (0.116 g, 0.948 mmol) were added to a solution of **16** (1.35 g, 4.97 mmol) and **10** (0.73 g, 2.37 mmol) in CH_2Cl_2 (25 mL) at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, and was then stirred for 90 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.8:0.2) gave **17** (1.43 g, 74%) as a yellow oil. IR (neat): ν 3289 (≡C–H), 1731 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97 (t, J=3 Hz, 4H), 1.98 (m, 8H), 2.38 (m, 8H), 3.48 (s, 4H), 4.02 (t, J=6 Hz, 8H), 5.09 (d, J=3.5 Hz, 4H), 5.16 (s, 4H), 6.42 (t, J=2 Hz, 2H), 6.48 (d, J=2 Hz, 4H), 7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 15.1, 28.0, 41.4, 66.1, 66.8, 67.0, 68.9, 83.3, 101.2, 106.5, 106.6, 127.8, 128.1, 128.9, 135.6, 137.3, 160.1, 166.1. Anal. Calcd for $C_{48}H_{50}O_{12}$: C, 70.40; H, 6.15. Found: C, 69.74; H, 6.31.

4.2.14. Compound **18**

DBU (0.38 mL, 2.55 mmol) was added to a stirred solution of C_{60} (400 mg, 0.55 mmol), I_2 (352 mg, 1.39 mmol), and **17** (454 mg, 0.55 mmol) in toluene (800 mL). The resulting solution was stirred for 12 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and concentrated. Column chromatography (SiO_2, CH_2Cl_2/hexane 1:1) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **18** (332 mg, 39%) as a dark-orange glassy product. IR (neat): ν 3292 (≡C–H), 1744 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 1.96 (m, 12H), 2.37 (m, 8H), 3.99 (t, J=6 Hz, 8H), 5.05 (d, J=13 Hz, 2H), 5.22 (d, J=12 Hz, 2H), 5.36 (d, J=12 Hz, 2H), 5.83 (d, J=13 Hz, 2H), 6.40 (t, J=2 Hz, 2H), 6.51 (d, J=2 Hz, 4H), 7.26 (m, 1H), 7.28 (m, 1H), 7.40 (m, 1H), 7.49 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 17.0, 28.1, 49.0, 66.2, 66.9, 67.4, 68.5, 69.0, 70.6, 83.4, 101.6, 107.3, 123.6, 125.2, 126.6, 128.2, 128.6, 129.0, 134.4, 135.8, 136.1, 136.6, 136.7, 137.8, 139.9, 141.0, 141.2, 142.3, 142.7, 143.2, 143.6, 143.8, 143.9, 144.1, 144.2, 144.3, 144.6, 144.9, 145.0, 145.2, 145.3, 145.6, 145.7, 145.8, 146.0, 147.3, 147.4, 148.6, 160.1, 162.6, 162.7. Anal. Calcd for $C_{108}H_{46}O_{12} \cdot 2CH_2Cl_2$: C, 77.47; H, 2.96. Found: C, 77.27; H, 2.57. FABMS: 1535 ($[M]^+$, calcd for $C_{108}H_{46}O_{12}$: 1535.55).

4.2.15. Compound **19**

To a mixture of **18** (65 mg, 0.042 mmol) and benzyl azide (28 mg, 0.21 mmol) in CH_2Cl_2 (1 mL) and H_2O (1 mL) were added $CuSO_4 \cdot 5H_2O$ (1 mg, 0.006 mmol) and sodium ascorbate (4 mg, 0.02 mmol). The reaction mixture was stirred for 20 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/MeOH 99:1) gave **19** (34 mg, 39%) as a dark-red glassy product. IR (neat): ν 1744 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.09 (m, 8H), 2.83 (t, J=7 Hz, 8H), 3.90 (t, J=6 Hz, 8H), 5.04 (d, J=13 Hz, 2H), 5.19 (d, J=12 Hz, 2H), 5.30 (d, J=12 Hz, 2H), 5.47 (s, 8H), 5.81 (d, J=13 Hz, 2H), 6.32 (t, J=2 Hz, 2H), 6.44 (d, J=2 Hz, 4H), 7.23 (m, 13H), 7.33 (m, 14H), 7.47 (t, J=2 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 22.2, 28.8, 29.7, 49.1, 54.0, 67.0, 68.5, 70.6, 101.5, 107.1, 120.8, 123.5, 126.6, 128.0, 128.6, 129.1, 134.4, 134.8, 135.7, 136.1, 136.6, 136.7, 137.7, 140.0, 141.1, 142.3, 142.7, 143.1, 143.5, 143.7, 143.9, 144.1, 144.2, 144.3, 144.6, 144.8, 144.9, 145.1, 145.3, 145.5, 145.6, 145.7, 146.0, 147.3, 147.4, 147.6, 148.6, 160.1, 162.5, 162.7. Anal. Calcd for $C_{136}H_{74}N_{12}O_{12} \cdot 3/2CHCl_3$: C, 73.49; H, 3.39; N, 7.48. Found: C, 73.46; H, 3.83; N, 7.05. MALDI-MS: 2068.6 ($[M]^+$, calcd for $C_{136}H_{74}O_{12}N_{12}$: 2068.16).

4.2.16. Compound **21**

DCC (2 g, 9.82 mmol), HOBt (cat), and DMAP (0.23 g, 1.87 mmol) were added to a solution of 3-bromopropan-1-ol (1.36 g, 9.82 mmol) and **10** (1.45 g, 4.68 mmol) in CH_2Cl_2 (50 mL) at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, and was then stirred for 90 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane 90:10) gave **21** (1.183 g, 46%) as a yellow oil. IR (neat): ν 1728 (C═O). ^1H NMR ($CDCl_3$, 300 MHz): δ 2.15 (m, 4H), 3.39 (t, J=6.5 Hz, 4H), 3.44 (s, 4H), 4.28 (t, J=6 Hz, 4H), 5.18 (s, 4H), 7.34 (m, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.05, 31.3, 41.4, 63.1, 66.8, 128.1, 128.4, 128.9, 135.6, 166.1.

4.2.17. Compound **22**

A mixture of **21** (1.016 g, 1.84 mmol) and NaN_3 (0.718 g, 11.04 mmol) in dry DMF (5 mL) was stirred at room temperature for

16 h. The organic layer was diluted with Et_2O, washed with water then brine, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2) gave **22** (668 mg, 76%) as a yellow oil. IR (neat): ν 2095 (–N_3), 1728 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.88 (m, 4H), 3.33 (t, J=6 Hz, 4H), 3.44 (s, 4H), 4.22 (t, J=6 Hz, 4H), 5.18 (s, 4H), 7.34 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 27.9, 41.3, 47.8, 62.3, 66.8, 128.1, 128.3, 128.9, 135.6, 166.1. Anal. Calcd for $C_{20}H_{24}N_6O_8$: C, 50.42; H, 5.08. Found: C, 50.79; H, 4.97.

*4.2.18. Compound **23***

DBU (0.76 mL, 3.10 mmol) was added to a stirred solution of C_{60} (800 mg, 1.1 mmol), I_2 (704 mg, 1.39 mmol), and **22** (908 mg, 1.1 mmol) in toluene (1600 mL). The resulting solution was stirred for 12 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane 60:40) followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2) gave **23** (214 mg, 16%) as a dark-orange glassy product. IR (neat): ν 2094 (–N_3), 1739 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (m, 4H), 3.41 (t, J=6 Hz, 4H), 4.44 (m, 4H), 5.19 (d, J=13 Hz, 2H), 5.87 (d, J=13 Hz, 2H), 7.30–7.44 (m, 3H), 7.53 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.0, 29.6, 47.9, 49.0, 49.2, 63.9, 66.9, 67.5, 70.5, 124.1, 126.9, 128.7, 135.8, 136.1, 136.5, 140.0, 141.0, 141.4, 142.3, 142.8, 143.3, 143.6, 143.8, 144.0, 144.2, 144.3, 144.4, 144.7, 145.0, 145.3, 145.4, 145.7, 145, 146.0, 146.1, 147.4, 147.5, 147.6, 148.5, 162.7, 162.9.

*4.2.19. Compound **24***

A mixture of **23** (84 mg, 0.07 mmol), phenylacetylene (15.8 mg, 0.15 mmol), $CuSO_4\cdot 5H_2O$ (1 mg, 0.006 mmol), and sodium ascorbate (4 mg, 0.02 mmol) in CH_2Cl_2 (3 mL) and H_2O (3 mL) was stirred at room temperature for 24 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.5:0.5) gave **24** (80 mg, 78%) as a dark-orange glassy product. IR (neat): ν 1742 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.41 (m, 4H), 4.42 (m, 4H), 4.50 (t, J=7 Hz, 4H), 5.30 (d, J=13 Hz, 2H), 5.87 (d, J=13 Hz, 2H), 7.30–7.44 (m, 9H), 7.55 (s, 1H), 7.75 (s, 2H), 7.77–7.84 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.3, 29.6, 30.9, 46.7, 63.4, 67.7, 119.9, 124.5, 125.7, 127.2, 128.2, 128.8, 130.4, 135.6, 135.8, 136.5, 138.1, 140.1, 141.0, 141.4, 142.3, 142.8, 143.4, 143.6, 143.9, 144.1, 144.2, 144.4, 144.7, 144.9, 145.0, 145.1, 145.3, 145.4, 145.5, 145.7, 145.8, 146.0, 146.1, 146.2, 147.6, 147.9, 148.4, 162.7, 163.0. Anal. Calcd for $C_{96}H_{32}N_6O_8\cdot CHCl_3$: C, 76.88; H, 2.20; N, 5.55. Found: C, 76.31; H, 2.19; N, 5.20. FABMS: 1397 ([M]$^+$, calcd for $C_{96}H_{32}N_6O_8$: 1397.35).

*4.2.20. Compound **25***

A mixture of **23** (50 mg, 0.031 mmol), **8** (209 mg, 0.15 mmol), $CuSO_4\cdot 5H_2O$ (0.5 mg, 0.003 mmol), and sodium ascorbate (2 mg, 0.009 mmol) in CH_2Cl_2 (1 mL) and H_2O (1 mL) was stirred at room temperature for 1 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.5:0.5) gave **25** (81 mg, 50%) as a dark-red glassy product. IR (neat): ν 1743 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J=7 Hz, 12H), 1.24 (m, 72H), 1.72 (m, 8H), 2.20 (m, 4H), 2.35 (m, 4H), 2.86 (t, J=7 Hz, 4H), 3.87 (t, J=6 Hz, 8H), 4.38 (m, 4H), 4.42 (t, J=7 Hz, 4H), 4.50 (t, J=6 Hz, 4H), 5.27 (d, J=13 Hz, 2H), 5.43 (s, 4H), 5.88 (d, J=13 Hz, 2H), 6.38 (t, J=2 Hz, 2H), 6.58 (d, J=2 Hz, 4H), 7.30–7.44 (m, 5H), 7.50 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 21.9, 22.6, 26.1, 28.0, 29.2, 29.3, 29.4, 29.6, 29.7, 31.9, 46.5, 49.1, 51.9, 63.4, 66.4, 66.8, 67.7, 68.1, 68.9, 70.5, 71.4, 101.7, 107.2, 121.4, 124.2, 127.1, 128.8, 134.3, 135.7, 136.0, 136.5, 138.0, 138.6, 139.2, 140.1, 140.8, 140.9, 141.0, 141.4, 141.7, 141.8, 142.1, 142.3, 142.8, 142.9, 142.95, 142.97, 142.99, 143.05, 143.3, 143.6, 145.7, 143.8, 143.9, 144.1, 144.2, 144.4, 144.45, 144.5, 144.55, 144.6, 144.62, 144.65, 144.7, 144.8, 144.9, 144.96, 144.97, 145.1, 145.14, 145.19, 145.23, 145.29, 145.5, 145.6, 145.7, 145.9, 146.1, 146.5, 147.3, 147.5, 147.6, 148.4, 160.4, 162.6, 162.9, 163.4. Anal. Calcd for $C_{278}H_{144}N_6O_{20}\cdot 2CHCl_3$: C, 81.54; H, 3.57; N, 2.04. Found: C, 81.60; H, 3.15; N, 2.22. MALDI-TOF-MS: 3889 ([MH]$^+$, calcd for $C_{278}H_{145}N_6O_{20}$: 3889.24).

*4.2.21. Compound **28***

A mixture of 3,5-dihydroxybenzyl alcohol (0.549 g, 3.917 mmol), **27** (2 g, 7.835 mmol), K_2CO_3 (2.97 g, 21.54 mmol), and LiBr (0.51 g, 5.87 mmol) in dry DMF (10 mL) was stirred at 80 °C for 60 h. The mixture was cooled to room temperature, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2) gave **28** (480 mg, 40%) as a yellow oil. IR (neat): ν 2091 (–N_3), 3362 (O–H). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.03 (m, 4H), 3.49 (t, J=6.5 Hz, 4H), 4.02 (t, J=6 Hz, 4H), 4.60 (s, 2H), 6.37 (t, J=2 Hz, 1H), 6.51 (d, J=2 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.7, 48.2, 64.5, 65.1, 100.6, 105.2, 143.5, 159.9. Anal. Calcd for $C_{13}H_{18}N_6O_3$: C, 50.97; H, 5.92. Found: C, 50.77; H, 5.57.

*4.2.22. Compound **29***

DCC (695 mg, 3.4 mmol), HOBt (cat), and DMAP (79 mg, 0.65 mmol) were added to a solution of **28** (990 mg, 3.23 mmol) and **10** (501 mg, 1.62 mmol) in CH_2Cl_2 (20 mL) at 0 °C. After 1 h, the mixture was allowed to warm slowly to room temperature, and was then stirred for 72 h, filtered, and evaporated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.5:0.5) gave **29** (694 mg, 48%) as a yellow oil. IR (neat): ν 2093 (–N_3), 1731 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.02 (m, 8H), 3.49 (t, J=6 Hz, 8H), 3.49 (s, 4H), 4.01 (t, J=6 Hz, 8H), 5.10 (s, 4H), 5.16 (s, 4H), 6.41 (t, J=2 Hz, 2H), 6.49 (d, J=2 Hz, 4H), 7.31 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.6, 41.4, 48.1, 64.6, 66.8, 66.9, 101.2, 106.6, 127.7, 128.1, 128.9, 135.6, 137.5, 159.9, 166.1, 166.15. Anal. Calcd for $C_{40}H_{46}N_{12}O_{12}$: C, 70.40; H, 6.15. Found: C, 69.74; H, 6.31.

*4.2.23. Compound **30***

DBU (0.38 mL, 2.55 mmol) was added to a stirred solution of C_{60} (400 mg, 0.55 mmol), I_2 (352 mg, 1.39 mmol), and **29** (492 mg, 0.55 mmol) in toluene (800 mL). The resulting solution was stirred for 12 h, then filtered through a short plug of SiO_2 (CH_2Cl_2) and evaporated. Column chromatography (SiO_2, CH_2Cl_2/hexane 80:20) followed by gel permeation chromatography (Biobeads SX-1 CH_2Cl_2) gave **30** (88 mg, 10%) as a dark-orange glassy product. IR (neat): 2093 (–N_3), 1743 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 2.00 (m, 8H), 3.47 (t, J=6 Hz, 8H), 3.96 (t, J=6 Hz, 8H), 5.06 (d, J=13 Hz, 2H), 5.24 (d, J=12 Hz, 2H), 5.35 (d, J=12 Hz, 2H), 5.82 (d, J=13 Hz, 2H), 6.38 (t, J=2 Hz, 2H), 6.51 (d, J=2 Hz, 4H), 7.18 (m, 1H), 7.39 (m, 1H), 7.49 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 28.7, 48.2, 49.0, 63.9, 64.6, 67.4, 68.5, 101.7, 107.4, 107.5, 123.6, 123.8, 125.3, 126.6, 126.7, 128.2, 128.6, 129.0, 134.4, 135.8, 136.1, 136.5, 136.6, 136.8, 137.8, 140.0, 140.9, 141.1, 141.3, 142.3, 142.7, 143.1, 143.6, 143.8, 144.0, 144.1, 144.2, 144.3, 144.6, 144.8, 145.0, 145.2, 145.4, 145.6, 145.7, 145.8, 145.9, 146.0, 147.3, 147.5, 148.6, 148.7, 148.75, 159.9, 162.6, 162.7.

*4.2.24. Compound **31***

To a mixture of **30** (50 mg, 0.031 mmol) and **8** (209.4 mg, 0.15 mmol) in CH_2Cl_2 (1 mL) and H_2O (1 mL) were added $CuSO_4\cdot 5H_2O$ (0.5 mg, 0.003 mmol) and sodium ascorbate (2 mg, 0.009 mmol). The reaction mixture was stirred for 1 h. The organic layer was diluted with CH_2Cl_2, washed with water, dried over $MgSO_4$, and concentrated. Column chromatography (SiO_2, CH_2Cl_2/methanol 99.5:0.5) gave **31** (34%) as a dark-red glassy product. IR (neat): 1743 (C=O). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.87 (t, J=7 Hz, 28H), 1.24 (s, 126H), 1.62 (s, 14H), 1.72 (m, 16H), 2.20 (t, J=6 Hz, 8H), 2.31 (t, J=6 Hz, 8H), 2.86 (m, 8H), 3.87 (t, J=6 Hz, 24H), 4.49 (m, 16H), 5.05 (d, J=13 Hz, 2H), 5.42 (s, 8H), 5.85 (d, J=13 Hz, 2H), 6.32 (m, 1H), 6.38 (d, J=2 Hz, 4H), 6.46 (m, 2H), 6.46 (d, J=2 Hz, 8H), 6.57 (d, J=2 Hz, 4H), 7.48 (m, 3H), 7.91 (s, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 14.1, 21.9, 22.7, 24.9, 25.5, 26.1, 28.0, 29.2, 29.3, 29.4, 29.6, 29.7, 29.9, 31.9, 33.9, 46.9, 64.4, 66.4, 68.1, 69.0, 71.4, 101.7, 107.2, 121.5, 135.7, 136.0, 136.5, 137.1, 138.6, 139.2, 139.6, 140.0, 140.1, 140.3, 140.8, 140.9, 141.0, 141.7, 141.8, 142.1, 142.9, 142.9, 143.6, 143.8, 144.4, 144.5, 144.6, 144.65, 144.8, 144.9, 145.1,

145.2, 145.4, 145.6, 146.1, 146.3, 146.9, 147.4, 147.5, 148.3, 148.5, 159.7, 160.5, 162.6, 163.4. Anal. Calcd for $C_{496}H_{290}N_{12}O_{36}\cdot CHCl_3$: C, 83.92; H, 4.12; N, 2.36. Found: C, 83.67; H, 4.30; N, 2.62. MALDI-TOF: 6994.5 ($[MH]^+$, calcd for $C_{496}H_{291}N_{12}O_{36}$: 6994.83).

Acknowledgements

This research was supported by the *Centre National de la Recherche Scientifique* (UMR 7509), the French Ministry of Research (doctoral fellowship to J.I.), and the *Conselho Nacional de Desenvolvimento Científico e Tecnológico* (Brazil). We further thank A. Saquet for the CV and OSWV measurements.

References and notes

1. Hirsch, A.; Brettreich, M. Fullerenes—Chemistry and Reactions. In *Fullerenes: principles and applications*; Langa, F., Nierengarten, J.-F., Eds.; RSC Nanoscience and Nanotechnology Series, 2007; Wiley-VCH: Weinheim, 2005.
2. (a) Segura, J. L.; Martín, N.; Guldi, D. M. *Chem. Soc. Rev.* **2005**, *34*, 31–37; (b) Nierengarten, J.-F. *New J. Chem.* **2004**, *28*, 1177–1191; (c) Figueira-Duarte, T. M.; Gégout, A.; Nierengarten, J.-F. *Chem. Commun.* **2007**, 109–119.
3. Da Ros, T.; Prato, M. *Chem. Commun.* **1999**, 663–669.
4. Diederich, F.; Isaacs, L.; Philp, D. *Chem. Soc. Rev.* **1994**, 243–255.
5. For selected examples, see: (a) Timmerman, P.; Anderson, H. L.; Faust, R.; Nierengarten, J.-F.; Habicher, T.; Seiler, P.; Diederich, F. *Tetrahedron* **1996**, *52*, 4925–4947; (b) Nierengarten, J.-F.; Schall, C.; Nicoud, J.-F.; Heinrich, B.; Guillon, D. *Tetrahedron Lett.* **1998**, *39*, 5747–5750; (c) Felder, D.; Gutiérrez Nava, M.; del Pilar Carreon, M.; Eckert, J.-F.; Luccisano, M.; Schall, C.; Masson, P.; Gallani, J.-L.; Heinrich, B.; Guillon, D.; Nierengarten, J.-F. *Helv. Chim. Acta* **2002**, *85*, 288–319; (d) Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F. *Tetrahedron Lett.* **1999**, *40*, 269–272; (e) Nierengarten, J.-F.; Felder, D.; Nicoud, J.-F. *Tetrahedron Lett.* **2000**, *41*, 41–44; (f) Gutiérrez-Nava, M.; Nierengarten, H.; Masson, P.; Van Dorsselaer, A.; Nierengarten, J.-F. *Tetrahedron Lett.* **2003**, *44*, 3043–3046; (g) Hahn, U.; Elhabiri, M.; Trabolsi, A.; Herschbach, H.; Leize, E.; Van Dorsselaer, A.; Albrecht-Gary, A.-M.; Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2005**, *44*, 5338–5341.
6. For selected examples, see: (a) Nierengarten, J.-F.; Herrmann, A.; Tykwinski, R. R.; Rüttimann, M.; Diederich, F.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 293–316; (b) Nierengarten, J.-F.; Eckert, J.-F.; Rio, Y.; Carreon, M. P.; Gallani, J.-L.; Guillon, D. *J. Am. Chem. Soc.* **2001**, *123*, 9743–9748; (c) Armaroli, N.; Accorsi, G.; Felder, D.; Nierengarten, J. F. *Chem.—Eur. J.* **2002**, *8*, 2314–2323; (d) Cardinali, F.; Mamlouk, H.; Rio, Y.; Armaroli, N.; Nierengarten, J.-F. *Chem. Commun.* **2004**, 1582–1583; (e) Gutierrez-Nava, M.; Accorsi, G.; Masson, P.; Armaroli, N.; Nierengarten, J.-F. *Chem.—Eur. J.* **2004**, *10*, 5076–5086; (f) Nierengarten, J.-F.; Gu, T.; Hadziioannou, G.; Tsamouras, D.; Krasnikov, V. *Helv. Chim. Acta* **2004**, *87*, 2948–2966; (g) Hahn, U.; González, J. J.; Huerta, E.; Segura, M.; Eckert, J.-F.; Cardinali, F.; de Mendoza, J.; Nierengarten, J.-F. *Chem.—Eur. J.* **2005**, *11*, 6666–6672.
7. (a) Nierengarten, J.-F.; Schall, C.; Nicoud, J.-F. *Angew. Chem., Int. Ed.* **1998**, *37*, 1934–1936; (b) Nierengarten, J.-F.; Eckert, J.-F.; Felder, D.; Nicoud, J.-F.; Armaroli, N.; Marconi, G.; Vicinelli, V.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M.; Hadziioannou, G.; Krasnikov, V.; Ouali, L.; Echegoyen, L.; Liu, S.-G. *Carbon* **2000**, *38*, 1587–1598; (c) Nierengarten, J.-F.; Oswald, L.; Nicoud, J.-F. *Chem. Commun.* **1998**, 1545–1546; (d) Urbani, M.; Nierengarten, J.-F. *Tetrahedron Lett.* **2007**, *48*, 8111–8115.
8. (a) Hahn, U.; Gégout, A.; Duhayon, C.; Coppel, Y.; Saquet, A.; Nierengarten, J.-F. *Chem. Commun.* **2007**, 516–518; (b) Delavaux-Nicot, B.; Kaeser, A.; Hahn, U.; Gégout, A.; Brandli, P.-E.; Duhayon, C.; Coppel, Y.; Saquet, A.; Nierengarten, J.-F. *J. Mater. Chem.* **2008**, *18*, 1547–1554.
9. Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004–2021.
10. Iehl, J.; Pereira de Freitas, R.; Nierengarten, J.-F. *Tetrahedron Lett.* **2008**, *49*, 4063–4066.
11. See also: (a) Isobe, H.; Cho, K.; Solin, N.; Werz, D. B.; Seeberger, P. H.; Nakamura, E. *Org. Lett.* **2007**, *9*, 4611–4614; (b) Iehl, J.; Pereira de Freitas, R.; Delavaux-Nicot, B.; Nierengarten, J.-F. *Chem. Commun.* **2008**, 2450–2452.
12. (a) Huisgen, R. *Pure Appl. Chem.* **1989**, *61*, 613–628; (b) Huisgen, G.; Szeimies, W.; Moebius, L. *Chem. Ber.* **1967**, *100*, 2494–2507; (c) Tornøe, C. W.; Meldal, M. *Proceedings of the 2nd International and 17th American Peptide Symposium, Peptides: The Waves of the Future*; Lebl, M.; Houghten, R. A., Eds.; Kluwer Academic: Dordrecht, The Netherlands, San Diego, CA, 2001, pp 263–264; (d) Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2002**, *41*, 2596–2599.
13. For selected examples, see: (a) Ornelas, C.; Aranzaes, J. L.; Cloutet, E.; Alves, S.; Astruc, D. *Angew. Chem., Int. Ed.* **2007**, *46*, 872–877; (b) Helms, B.; Mynar, J. L.; Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15020–15021; (c) Wilkinson, B. L.; Bornaghi, L. F.; Poulsen, S.-A.; Houston, T. A. *Tetrahedron* **2006**, *62*, 8115–8125; (d) Lee, B.-Y.; Park, S. R.; Jeon, H. B.; Kim, K. S. *Tetrahedron Lett.* **2006**, *47*, 5105–5109; (e) Wu, P.; Feldman, A. K.; Nugent, A. K.; Hawker, C. J.; Scheel, A.; Voit, B.; Pyun, J.; Fréchet, J. M. J.; Sharpless, K. B.; Fokin, V. V. *Angew. Chem., Int. Ed.* **2004**, *43*, 3928–3932.
14. For selected examples, see: (a) Prato, M.; Li, Q. C.; Wudl, F.; Lucchini, V. *J. Am. Chem. Soc.* **1993**, *115*, 1148–1150; (b) Yamakoshi, Y. N.; Yagami, T.; Sueyoshi, S.; Miyata, N. *J. Org. Chem.* **1996**, *61*, 7236–7237; (c) Hawker, C. J.; Saville, P. M.; White, J. M. *J. Org. Chem.* **1994**, *59*, 3503–3505; (d) Yashiro, A.; Nishida, Y.; Ohno, M.; Eguchi, S.; Kobayashi, K. *Tetrahedron Lett.* **1998**, *39*, 9031–9034.
15. Bingel, C. *Chem. Ber.* **1993**, *126*, 1957–1959.
16. Cardullo, F.; Seiler, P.; Isaacs, L.; Nierengarten, J.-F.; Haldimann, R. F.; Diederich, F.; Mordasini-Denti, T.; Thiel, W.; Boudon, C.; Gisselbrecht, J.-P.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 343–371.
17. (a) Nierengarten, J.-F.; Gramlich, V.; Cardullo, F.; Diederich, F. *Angew. Chem., Int. Ed.* **1996**, *35*, 2101–2103; (b) Nierengarten, J.-F.; Habicher, T.; Kessinger, R.; Cardullo, F.; Diederich, F.; Gramlich, V.; Gisselbrecht, J.-P.; Boudon, C.; Gross, M. *Helv. Chim. Acta* **1997**, *80*, 2238–2276.
18. Zhang, S.; Rio, Y.; Cardinali, F.; Bourgogne, C.; Gallani, J.-L.; Nierengarten, J.-F. *J. Org. Chem.* **2003**, *68*, 9787–9797 and references therein.
19. Armaroli, N.; Barigelletti, F.; Ceroni, P.; Eckert, J.-F.; Nicoud, J.-F.; Nierengarten, J.-F. *Chem. Commun.* **2000**, 599–600.
20. Echegoyen, L.; Echegoyen, L. E. *Acc. Chem. Res.* **1998**, *31*, 593–601.
21. (a) Felder, D.; Nierengarten, H.; Gisselbrecht, J. P.; Boudon, C.; Leize, E.; Nicoud, J. F.; Gross, M.; Van Dorsselaer, A.; Nierengarten, J. F. *New J. Chem.* **2000**, *24*, 687–695; (b) Hahn, U.; Maisonhaute, E.; Amatore, C.; Nierengarten, J.-F. *Angew. Chem., Int. Ed.* **2007**, *46*, 951–954.