Tetrahedron Letters 50 (2009) 398–401

Contents lists available at ScienceDirect

Tetrahedron Letters

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

Regioselective triphenylamine-tether-directed synthesis of [60]fullerene bis-adducts

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ARTICLE INFO

Article history:
Received 29 August 2008
Revised 27 October 2008
Accepted 7 November 2008
Available online 12 November 2008

ABSTRACT

The tether-directed regioselective synthesis of equatorial bis-adducts of [60]fullerene via the 1,3-dipolar cycloaddition reaction of azomethine ylides is reported. A mono-[60]fulleropyrrolidine adduct, derived via 1,3-dipolar cycloaddition of azomethine ylides generated in situ upon thermal condensation of triphenylamine bis-aldehyde and an α-amino acid, was isolated and further reacted to yield, exclusively and selectively, the equatorial bis-adduct, which is structurally characterized by appropriate spectroscopic means.

1. Introduction

Tether-directed functionalization of fullerenes is a method of choice for the regioselective formation of multi-adducts.[1] The novelty of the method is that it offers the possibility for the synthesis of specific fullerene bis-adducts (or multi-adducts), in moderate to high yields, that are otherwise difficult and/or improbable to obtain under standard, thermodynamically and/or kinetically controlled reaction conditions.

The 1,3-dipolar cycloaddition of azomethine ylides to fullerenes is a powerful methodology for the preparation of nanosized hybrid materials suitable for diverse applications.[2] Therefore, it is not surprising that stepwise bis-cycloaddition of symmetric azomethine ylides onto the skeleton of [60]fullerene has led to a mixture of all possible eight bis-adducts. HPLC separation of the bis-adduct mixture into single isomers has also been achieved.[3]

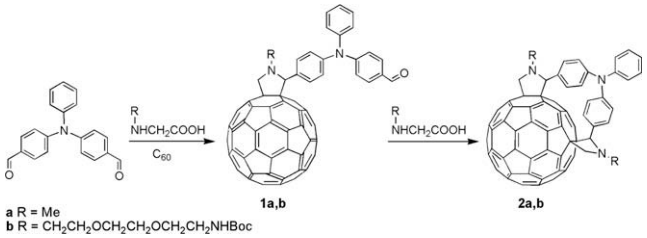
The use of a tether in the 1,3-dipolar cycloaddition of azomethine ylides to [60]fullerene has already been employed. However, the synthesis of mixtures containing bis-adduct isomers that have not been separated is reported,[4] while separation of such a mixture and characterization of isolated [60]fulleropyrrolidine tethered bis-adducts have only recently been achieved.[5]

Herein, we report on the regioselective synthesis of an equatorial [60]fullerene bis-adduct via cycloaddition of in situ generated azomethine ylides upon thermal condensation of triphenylamine (TPA) bis-aldehyde and an α-amino acid. The aim of the current work is two-fold, namely, (i) to incorporate the rigid TPA moiety as a tether to direct, with full regioselectivity, the introduction of the second fused pyrrolidine unit at the fullerene sphere and, (ii) to prepare a new push-pull hybrid material consisting of the good electron acceptor [60]fullerene and electron donor TPA, which also serves as an efficient hole-transporter and electroluminescent material.[6–8]

2. Results and discussion

Our approach for the tether-directed regioselective formation of [60]fullerene bis-adducts is based on a two-step mono-addition reaction sequence of azomethine ylides onto [60]fullerene, in which TPA itself is utilized as a rigid tether. In the first step, 1,3-dipolar cycloaddition of azomethine ylides, generated in situ upon thermal condensation of TPA bis-aldehyde and sarcosine onto [60]fullerene, resulted in the mono-fulleropyrrolidine adduct having a free aldehyde unit. In the following step, further reaction with sarcosine resulted in the formation of the second fused pyrrolidine ring onto the fullerene sphere, with complete regioselectivity, at the equatorial position (Scheme 1).

In a typical experiment, when a toluene solution of [60]fullerene was treated at reflux with 1 equiv of 4,4′-diformyltriphenylamine[9] and 10 equiv of sarcosine for 2.5 h, the mono-adduct **1a**, having a free aldehyde, was obtained in 31% yield (76% based on recovered [60]fullerene) after column chromatography. At this point, it should be emphasized that performing the reaction with either an excess of TPA bis-aldehyde (2.5 equiv) and/or higher



Scheme 1. Synthetic route of TPA-bridged [60]fullerene bis-adducts.

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0040-4039/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2008.11.022

temperature/shorter reaction time conditions (i.e., refluxing chlorobenzene for 15 min) did not have a positive effect on the yield of **1a**.

Upon thermal treatment of mono-adduct **1a** with sarcosine (5 equiv) in *o*-dichlorobenzene (DCB) at 133 °C, bis-adduct **2a** was formed in 30% yield (41% yield based on recovered **1a**). Similar results were obtained in refluxing chlorobenzene. In general, temperatures greater than 120 °C are ideal for the formation of the bis-adduct (i.e., very poor results were obtained in toluene); however, special caution is needed as extensive degradation occurs at temperatures above 140 °C.

As **2a** was insoluble in polar solvents and showed limited solubility even in carbon disulfide, a more polar α-amino acid was employed in the azomethine ylide reaction with [60]fullerene. Thus, we were able to perform a complete spectroscopic characterization and study of the so-formed bis-adduct. Reaction of [60]fullerene with TPA bis-aldehyde (2 equiv) and *tert*-butoxy carbonyl (Boc)-((aminoethoxy)ethoxy)ethyl (AEE) N-substituted glycine[10] (1 equiv), in refluxing toluene for 15 min, afforded the mono-adduct **1b** in 33% yield (62% based on recovered [60]fullerene). In the following step, **1b** was treated with Boc–AEE–glycine (4 equiv) in refluxing toluene for 30 min to provide the bis-adduct **2b** in 35% yield (53% based on recovered **1b**). At this stage, the following points should be highlighted: (i) **2b** is very soluble in chloroform and DMF, in contrast to **2a** which shows limited solubility, (ii) reactions leading to **2b** were faster and took place at lower temperatures compared to those applied for the synthesis of **2a**, which is most likely rationalized to the better solubility of the α-amino acid utilized and, (iii) HPLC (Japan Analytical Industry Co Ltd, utilizing a Buckyprep 20 × 250 column with toluene as eluent at 10 mL/min flow rate) for the purification of **1b** and **2b** is preferable.

Attempts to synthesize bis-adducts **2a** and **2b** in one-step, that is, directly from [60]fullerene without isolating the corresponding mono-adduct, were not successful. Competitive formation of a dimer, as well as degradation, polymerization and/or multiaddition reactions occurred, resulting in the formation of inseparable and complex mixtures in very low yields.

In the ^{1}H NMR spectra of the bis-adducts, each proton of the TPA phenyl rings adjacent to the fullerene core showed a unique chemical shift. This is in sharp contrast to the AA′XX′ patterns of the mono-adducts as shown in Figure 1. The two pyrrolidine rings showing characteristic patterns are discernible, for example, in the spectrum of **2a**, a pair of doublets at 4.14 ppm and 4.86 ppm ($|^2J|$ = 9.3 Hz) and a singlet at 4.60 ppm resembling the pyrrolidine signals of the mono-adduct **1a** (as doublets at 4.30 ppm and 4.99 ppm with $|^2J|$ = 9.3 Hz and a singlet at 4.96 ppm) were evident, while the second pyrrolidine appears as a pair of doublets at 4.82 ppm and 5.05 ppm ($|^2J|$ = 12.3 Hz) and a much less shielded singlet at 6.17 ppm. The corresponding ^{1}H NMR spectra of mono-adduct **1b** and bis-adduct **2b** are presented in the Supplementary data (Figs. S1 and S2). The limited solubility of **2a** hindered our attempts to record a suitable ^{13}C NMR spectrum; however, we were able to record the ^{13}C NMR spectrum of mono-adduct **1a,** as well as that of **1b** (Supplementary data, Figs. S3 and S4). However, as previously mentioned, the enhanced solubility obtained for bis-adduct **2b** allowed us to record the ^{13}C NMR spectrum (Fig. 1). A total of 71 signals in the sp^2 region between 160 and 114 ppm were found, as well as 23 signals in the sp^3 region, between 81 and 28 ppm. Combination of the ^{13}C and ^{1}H NMR measurements indicates that bis-adduct **2b** possesses C_1 molecular symmetry. Apparently, the bis-adduct is nonsymmetric, having two chiral centres in the pyrrolidine rings, with the structure shown in Scheme 1 being a racemate.[5]

In the attenuated-total-reflectance infra-red (ATR-IR) spectra of **2b**, the characteristic peaks for the protecting Boc carbonyl (1708 cm^{-1}) and NH (3438 cm^{-1} and 3342 cm^{-1}) groups were evident (Supplementary data, Fig. S5). Moreover, in both the mono- and bis-adducts, the C–H stretching vibrations (3030–2800 cm^{-1}) as well as the characteristic absorptions for fullerenes were also present.

Matrix-assisted-laser-desorption-ionization time-of-flight mass-spectrometry (MALDI-TOF-MS), in the negative ionization mode, showed molecular ion peaks for both the mono- and bis-adducts (Supplementary data, Figs. S6 and S7). As commonly observed in fullerene derivatives, the molecular ion peak was accompanied by an intense peak at m/z = 720, corresponding to the C_{60} fragment.

In the electronic absorption (UV–vis) spectra of monoadducts **1a** and **1b** obtained in toluene, the characteristic absorptions of a

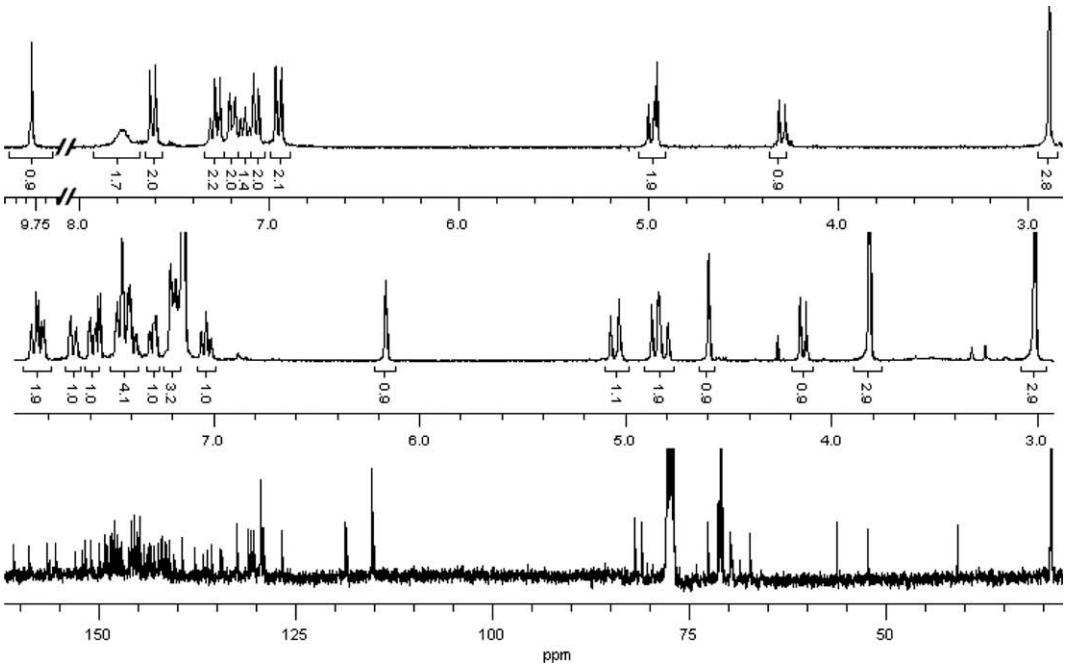

Figure 1. ^{1}H NMR (300 MHz) spectra of mono-adduct **1a** (top, 50% CS_2/$CDCl_3$) and bis-adduct **2a** (middle, CS_2) and the ^{13}C NMR (125 MHz, $CDCl_3$) spectrum of bis-adduct **2b** (bottom).

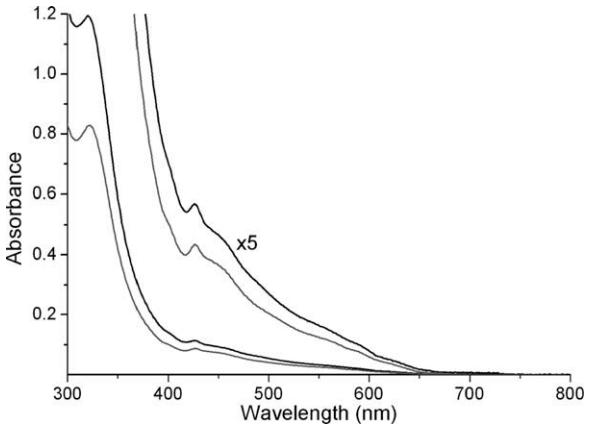

Figure 2. UV–vis absorption spectra of **2a** (black) and **2b** (grey), obtained in toluene.

fulleropyrrolidine at 433 nm and that of the TPA unit in the UV region were evident (Supplementary data, Fig. S8). Fullerene bis-adducts **2a** and **2b** showed spectra possessing the pattern of equatorial bis-addition[11] onto the fullerene core (Fig. 2). The latter is in full accordance with the absence of molecular symmetry, a result already demonstrated by the NMR measurements.

Preliminary photophysical studies of the bis-adducts were also performed. In this context, the steady-state fluorescence emission spectra of **2b** in an apolar (toluene) and a polar (DMF) solvent were recorded upon excitation of the fullerene moiety at 430 nm (Fig. 3). The insolubility of **2a** in DMF precluded such measurement. The fluorescence emission of **2b** observed at 778 nm with a shoulder at 710 nm in toluene (fulleropyrrolidine bis-adducts are reported to emit in this region[12]) appeared red-shifted (789 nm with a shoulder at 720 nm), broadened and depressed in the DMF solution. Such a solvatochromic red-shift suggests stabilization of the excited-state in polar media, whereas fluorescence emission quenching suggests electron transfer processes towards a charge-separated state. Further photophysical measurements, which are currently underway, are expected to shed light on the actual mechanism of the charge transfer phenomena.

In conclusion, the tether-directed regioselective bis-addition of TPA bis-aldehyde onto [60]fullerene was demonstrated. It was shown that in a two-step cycloaddition reaction sequence, the presence of the rigid TPA moiety directs the second pyrrolidine unit fused onto the fullerene sphere exclusively at the equatorial position. Interestingly, the performance of the second cycloaddition reaction onto the fullerene core with a different α-amino acid than that utilized in the first step allows the preparation of novel hybrid bis-fullerene adducts. Experiments along these lines are currently underway in our laboratories and the results will be reported in due course.

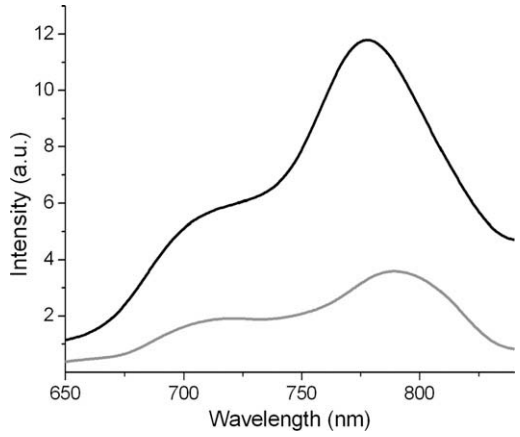

Figure 3. Steady-state fluorescence spectra of bis-adduct **2b**, obtained in toluene (black) and DMF (grey); λ_{ex} = 430 nm.

3. Experimental

3.1. Mono-adduct 1a

A mixture of C_{60} (100 mg, 0.139 mmol), sarcosine (124 mg, 1.39 mmol) and 4,4′-diformyltriphenylamine (42 mg, 0.139 mmol) in toluene (100 mL) was stirred at reflux for 2.5 h. After cooling, petroleum ether (65 mL) was added, and the mixture was subjected to column chromatography (silica gel) using 40% petroleum ether/toluene to collect unreacted C_{60} (40 mg, 67%), toluene (traces of bis-adduct and dumbbell dimer) and finally 2% ethyl acetate/toluene to yield **1a** as a dark red solid (45 mg, 31%). ATR-IR (neat): ν(cm^{-1}) 3032, 2948, 2919, 2781, 1689, 1586, 1505, 1488, 1463, 1427, 1317, 1283, 1268, 1216, 1159, 1124, 1105, 903, 821, 725, 692, 552; ^{1}H NMR (300 MHz, 50% CS_2/$CDCl_3$): δ (ppm) 2.89 (s, 3H), 4.30 (d, J = 9.3 Hz, 1H), 4.96 (s, 1H), 4.99 (d, J = 9.3 Hz, 1H), 6.92–6.97 (AA′XX′, 2H), 7.04–7.08 (AA′XX′, 2H), 7.12 (t, J = 7.2 Hz, 1H), 7.17–7.21 (AA′XX′, 2H), 7.25–7.31 (m, 2H), 7.59–7.63 (AA′XX′, 2H), 7.77 (br s, 2H), 9.77 (s, 1H); ^{13}C NMR (75 MHz, 50% CS_2/$CDCl_3$): δ (ppm) 189.28, 156.12, 153.79, 153.20, 153.09, 152.71, 147.35, 147.32, 146.66, 146.43, 146.43, 146.35, 146.34, 146.33, 146.26, 146.23, 146.15, 146.00, 145.96, 145.75, 145.65, 145.55, 145.51, 145.43, 145.40, 145.35, 145.33, 145.29, 145.19, 145.18, 144.76, 144.67, 144.44, 144.37, 143.25, 143.09, 142.76, 142.70, 142.66, 142.66, 142.29, 142.27, 142.21, 142.14, 142.11, 142.09, 142.02, 142.02, 141.79, 141.73, 141.68, 140.29, 140.25, 140.01, 139.17, 136.84, 136.53, 136.02, 135.77, 133.69, 131.23, 130.49, 129.85, 129.68, 126.12, 126.04, 125.18, 119.96, 82.90, 77.32, 70.06, 68.89, 40.11; MALDI-TOF MS calcd for $C_{82}H_{20}N_2O$: 1048, found: m/z 1049 [M+H]$^+$.

3.2. Bis-adduct 2a

A mixture of **1a** (30 mg, 0.029 mmol) and sarcosine (13 mg, 0.143 mmol) in o-dichlorobenzene (30 mL) was stirred at 133 °C for 45 min. After cooling, the mixture was subjected to column chromatography using o-dichlorobenzene to collect **2a** as a dark red solid (9 mg, 30%), followed by 2% ethyl acetate/toluene to collect unreacted **1a** (8 mg, 26%). ATR-IR (neat): ν(cm^{-1}) 3026, 2942, 2779, 1592, 1504, 1492, 1455, 1328, 1227, 1177, 1101, 856, 820, 739, 690, 551; ^{1}H NMR (300 MHz, CS_2, C_6D_6 insert as external lock): δ (ppm) 3.02 (s, 3H), 3.82 (s, 3H), 4.14 (d, J = 9.3 Hz, 1H), 4.60 (s, 1H), 4.82 (d, J = 12.3 Hz, 1H), 4.86 (d, J = 9.3 Hz, 1H), 5.05 (d, J = 12.3 Hz, 1H), 6.17 (s, 1H), 7.04 (t, J = 7.2 Hz, 1H), 7.15–7.21 (m, 3H), 7.30 (dd, J = 8.3, 1.6 Hz, 1H), 7.37–7.47 (m, 4H), 7.59 (dd, J = 8.3, 1.9 Hz, 1H), 7.69 (dd, J = 8.4, 1.9 Hz, 1H), 7.83–7.89 (m, 2H); MALDI-TOF MS calcd for $C_{84}H_{25}N_3$: 1075, found: m/z 1077 [M+2H]$^+$.

3.3. Mono-adduct 1b

A mixture of C_{60} (100 mg, 0.139 mmol), Boc–AEE–glycine (43 mg, 0.139 mmol) and 4,4′-diformyltriphenylamine (84 mg, 0.278 mmol) in toluene (100 mL) was stirred at reflux for 15 min. After cooling, the mixture was subjected to column chromatography using toluene to collect unreacted C_{60} (46 mg, 46%), 5–10% ethyl acetate/toluene (unreacted triphenylamine) and 20% ethyl acetate/toluene to collect the impure product which was further

purified by preparative HPLC (R_t = 14.37 min), resulting in **1b** as a dark red solid (58 mg, 33%). ATR-IR (neat): ν(cm^{-1}) 3444, 3344, 3029, 2973, 2924, 2801, 1706, 1690, 1585, 1503, 1489, 1459, 1427, 1318, 1270, 1159, 1107, 902, 821, 725, 695, 552; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 1.44 (s, 9H), 2.95 (dt, J = 11.8, 5.5 Hz, 1H), 3.31–3.36 (m, 2H), 3.54–3.62 (m, 3H), 3.72–3.75 (m, 2H), 3.80–3.86 (m, 2H), 4.00–4.12 (m, 2H), 4.32 (d, J = 9.6 Hz, 1H), 4.98 (br s, 1H), 5.18 (s, 1H), 5.21 (d, J = 9.6 Hz, 1H), 6.92–6.96 (AA′XX′, 2H), 7.06–7.09 (AA′XX′, 2H), 7.13 (t, J = 7.2 Hz, 1H), 7.17–7.21 (AA′XX′, 2H), 7.26–7.32 (m, 2H), 7.61–7.65 (AA′XX′, 2H), 7.77 (br s, 2H), 9.78 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 190.30, 156.37, 155.85, 153.99, 153.36, 153.09, 152.97, 147.30, 147.27, 146.67, 146.38, 146.26, 146.25, 146.17, 146.14, 146.08, 146.07, 145.93, 145.92, 145.67, 145.52, 145.47, 145.43, 145.41, 145.31, 145.28, 145.26, 145.20, 145.11, 144.70, 144.61, 144.38, 144.31, 143.17, 142.98, 142.67, 142.60, 142.55, 142.23, 142.20, 142.13, 142.12, 142.06, 142.03, 141.98, 141.96, 141.92, 141.67, 141.63, 141.59, 140.18, 140.10, 139.84, 139.00, 136.68, 136.42, 135.94, 135.64, 133.99, 131.23, 130.54, 129.66, 129.32, 126.17, 125.99, 125.02, 119.67, 81.72, 79.20, 76.45, 70.59, 70.45, 70.37, 70.21, 69.05, 67.63, 52.17, 40.35, 28.43; MALDI-TOF MS calcd for $C_{92}H_{39}N_3O_5$: 1266, found: m/z 1267 $[M+H]^+$.

3.4. Bis-adduct 2b

A mixture of **1b** (30 mg, 0.024 mmol) and Boc–AEE–glycine (14 mg, 0.048 mmol) in toluene (30 mL) was stirred at reflux for 30 min. After cooling, the mixture was subjected to column chromatography using 20% ethyl acetate/toluene to collect a mixture which was separated by preparative HPLC resulting in **2b** (R_t = 11.42 min, 13 mg, 35%) as a dark red solid, together with unreacted **1b** (10 mg, 34%). ATR-IR (neat): ν(cm^{-1}) 3438, 3342, 3030, 2971, 2920, 2863, 1708, 1593, 1503, 1493, 1456, 1362, 1244, 1164, 1110, 860, 820, 742, 692, 554; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.45 (s, 18H), 2.93 (dt, J = 11.8, 5.5 Hz, 1H), 3.30–3.34 (m, 4H), 3.45 (dt, J = 11.8, 5.5 Hz, 1H), 3.55 (t, J = 5.0 Hz, 2H), 3.59 (t, J = 5.0 Hz, 2H), 3.64–3.67 (m, 2H), 3.69–3.72 (m, 2H), 3.73–3.79 (m, 4H), 3.88–4.98 (m, 6H), 4.08–4.10 (m, 1H), 4.57 (s, 1H), 4.67 (d, J = 12.5 Hz, 1H), 4.79 (d, J = 12.5 Hz, 1H), 4.81 (d, J = 9.5 Hz, 1H), 4.96 (br s, 2H), 6.05 (s, 1H), 6.86 (t, J = 7.2 Hz, 1H), 6.97 (dd, J = 8.0, 1.9 Hz, 1H), 7.05–7.08 (m, 3H), 7.17 (dd, J = 8.2, 1.7 Hz, 1H), 7.23 (dd, J = 8.2, 1.7 Hz, 1H), 7.27–7.30 (m, 2H), 7.35 (dd, J = 8.3, 1.8 Hz, 1H), 7.47 (dd, J = 8.3, 1.8 Hz, 1H), 7.61–7.65 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 160.50, 158.32, 156.18, 155.92, 155.04, 152.72, 151.59, 151.30, 150.58, 150.54, 149.64, 148.86, 148.68, 148.54, 148.09, 147.90, 147.86, 147.65, 147.64, 147.55, 147.49, 147.07, 147.04, 146.77, 146.59, 145.90, 145.85, 145.58, 145.53, 145.46, 145.13, 144.83, 144.77, 144.71, 144.62, 144.48, 144.45, 144.16, 143.74, 143.28, 142.98, 142.89, 142.40, 142.15, 141.80, 141.77, 141.58, 141.57, 141.14, 141.05, 140.76, 140.69, 139.89, 138.85, 137.47, 136.26, 135.74, 135.14, 134.26, 133.98, 131.96, 130.63, 130.26, 130.03, 129.11, 128.97, 128.76, 128.54, 126.36, 118.24, 114.86, 81.25, 80.57, 79.93, 79.23, 77.21, 76.46, 75.82, 73.43, 72.19, 70.72, 70.52, 70.38, 70.37, 70.36, 70.33, 69.11, 68.04, 66.66, 65.16, 55.74, 51.74, 40.40, 28.45; MALDI-TOF MS calcd for $C_{104}H_{63}N_5O_8$: 1510, found: m/z 1510 $[M]^+$.

Acknowledgements

Partial financial support from the EU FP7, Capacities Program, NANOHOST project (GA 201729) and the EU FP6, Transfer of Knowledge (ToK) Program, FDPA project (MTKD-CT-2006-042488) is acknowledged. We are indebted to Dr. K. Porfyrakis at Oxford University for the MALDI-TOF-MS and to Dr. A. Panagiotopoulou at NCSR 'Democritos' for some initial NMR spectra.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.11.022.

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