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An Approach to Nanobioparticles – Synthesis and Characterization of Fulleropeptides

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Two sets of new peptides incorporating fulleropyrrolidine units – Fp-GABA$_n$-Gly$_m$-O*t*Bu – have been designed, synthesized and completely characterized. In the first series the chain contained only GABA (γ-aminobutyric) residues, whereas in the second one glycine moieties were also inserted as well as GABA. Most of the target compounds were prepared by DCC/DMAP-assisted coupling of previously synthesized GABA-containing fulleropyrrolidinic acid and corresponding *C*-protected small peptides, although for two fulleropeptides [3+2] cycloadditions of azomethine ylides to C_{60} were employed. All new compounds were characterized by standard spectroscopic methods. Complete assignments of peptide spin systems were achieved by extensive NMR analysis (^{1}H, ^{13}C, H,H-COSY, HSQC, HMBC and TOCSY).

Introduction

Because of its interesting physical and chemical properties C_{60} represents an attractive research target, but its widespread application is still limited by its quite low solubility in water and almost all organic solvents.[1] In order to increase fullerene solubility and to expand the scope of its applications, two methodologically different efforts have been developed. The first involves noncovalent encapsulation of C_{60} into cyclodextrins, calixarenes,[2] phospholipids,[3] micelles[4] or liposomes,[4] affording soluble complexes with no changes in the physical properties of the carbon core. The second approach, functionalization of C_{60}, remains the more commonly used way to improve solubility. Direct attachment of polar substituents to C_{60}[5] leads mainly to complex mixtures containing numerous isomers and compounds possessing different numbers of heteroatomic addends. In contrast, however, carbon-carbon bond-forming modifications of fullerenes, particularly cycloadditions,[6] take place much more selectively, affording well-defined products. The reactions mostly used for this purpose are S_Ni cyclopropanation (Bingel's reaction)[7] and [4+2][5] and [3+2] cycloadditions.[8] Functionalization also offers the potential for significant change in the physicochemical properties of derivatives, also widening the scope of their potential applications. In addition, the nanometer size of C_{60} is large enough to allow the synthesis of "smart" derivatives, the interactions of which with each other, with other molecules or with living organisms are governed by the properties of the introduced subunits. Such programmed functionalization can also make the fullerene core much more soluble, thus overcoming the main limitation to its application.

Because of the unique properties of C_{60}, many research domains – such as molecular machines,[9] new materials, bio-jymimics and medicinal chemistry – include a focus on fullero derivatives. Liquid crystal self-organization has been observed in some bis-dendritic fulleropyrrolidines,[10] whereas photoinduced electron transfer occurred in monofulleropyrolidines bearing dendritic and ferrocene[11] or porphyrin[12] subunits. Organofullerenes also showed promise in in vitro photodynamic treatment of human carcinoma cells[13] and DNA photocleavage,[14] and cell membrane protection might be expected due to the antioxidant properties.[15] The versatility of fullero derivatives is also illustrated by their ability to act as phospholipid mimetics[16] and drug carriers.[17] It is important to note that the fullerene derivatives usually exhibit lower toxicities than typical drugs.[18]

Amino acids and peptides are crucial building blocks of all living organisms and their conjugation with fullerene attracts a lot of scientific interest.[19–22] Syntheses of C_{60}-containing amino acids are mainly based on different addition reaction of suitable substrates to the fullerene (cyclopropanation,[23–25] [3+2][26–28] and [4+2] cycloadditions[29–31]). The biggest unnatural amino acid so far reported, fulleroproline, was obtained by 1,3-dipolar cycloaddition of an azomethine ylide to C_{60},[32] whereas a methanofullerene-substituted amino acid prepared by cyclopropanation of C_{60} was the starting material for the first fulleropeptide.[33]

The synthesis of fulleropeptides is mainly based on the coupling of various fullerene-containing amino acids with

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corresponding peptides under solution[33–37] or solid-phase[20,28,38] conditions. In previous research we showed that fulleropyrrolidinic acid **1** (Figure 1), incorporating γ-aminobutyric acid (GABA), could be easily and efficiently synthesized and also further transformed into steroidal esters.[15] Having a good precursor to hand, we anticipated that its coupling with amino acids and peptides could contribute to studies of fullerene-biomolecule nanoparticles. Designed compounds with improved solubility, even in the form of esters, represent good candidates for further investigation of fullerene-based bioactive compounds. Moreover, suitably positioned amide bonds containing both 1,4- and 1,6-carbonyl functions allow the possibility for additional examination of potential hydrogen-bond-induced host–guest interactions, as well as supramolecular and/or hierarchical self-organization. Thanks to the presence of the terminal bulky fullerene subunit, incorporation of designed compounds into more complex systems, such as mechanically interlocked structures, might also be expected. For that purpose, the assignment of all spin-active nuclei of the peptide backbone is considered a helpful tool able to facilitate further studies.

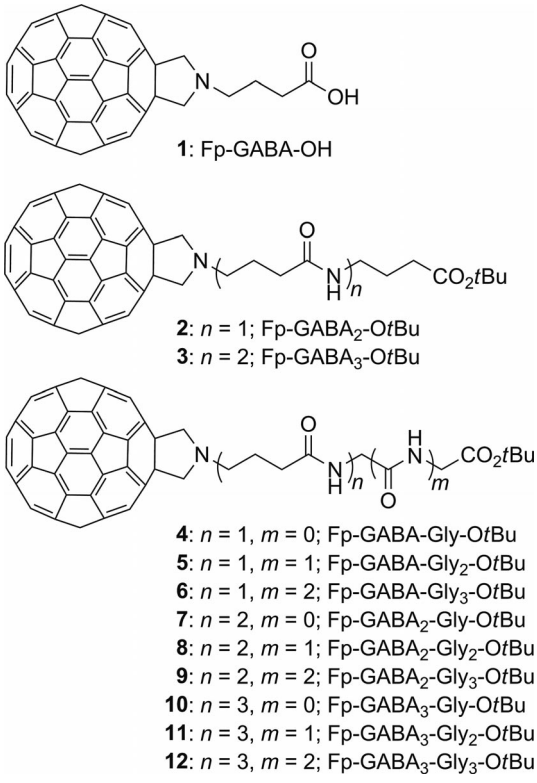


Figure 1. Target fulleropeptides **2**–**12** derived from fulleropyrrolidinic acid **1**.

Here we present the synthesis and complete characterization of two sets of new fulleropeptides: in the first series the side chains consist of repeating GABA units (**2** and **3**, Figure 1) and in the second, in addition to GABA, the simplest natural amino acid – glycine – was also incorporated, affording nine new fulleropyrrolidinic peptides Fp-GABA$_n$-Gly$_m$-O*t*Bu (n = 1–3, m = 0–2; **4**–**12**, Figure 1).

Results and Discussion

Chemistry

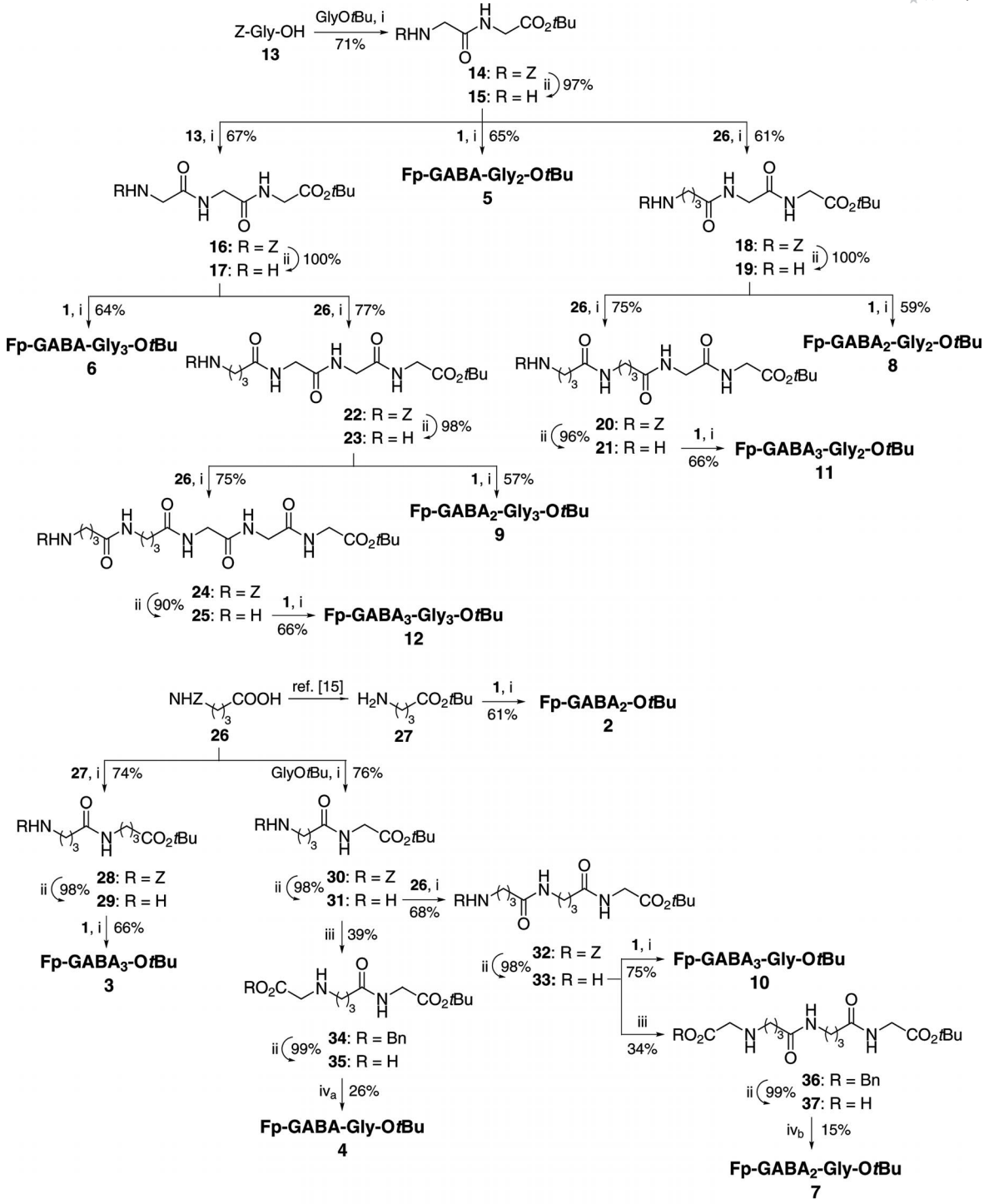
Most of the target compounds (nine out of 11) were successfully obtained from the previously prepared GABA-containing fulleropyrrolidinic acid (Fp-GABA-OH, **1**) and corresponding amines by a standard DCC/DMAP amidation procedure[39] (Scheme 1). Unexpectedly though, attempts to synthesize fulleropeptides **4** and **7** by this approach (with H-Gly-O*t*Bu and H-GABA-Gly-O*t*Bu) failed. No improvement was observed on prolonging the reaction time to 36 h, on increasing the reaction temperature from ambient to reflux, or with use of an excess of the appropriate peptidic amine. At the same time, these amino compounds easily underwent coupling with DCC-activated non-fullerenic acids (see Scheme 1, the preparation of the peptides **14**, **30** and **32**). As a consequence, an additional approach involving the generation of peptidic azomethine ylides and subsequent [3+2] cycloaddition to C_{60} was designed (Scheme 1).

Peptide Coupling with Fp-GABA-OH

Generally, step-by-step peptide elongation was achieved in good yields (59–77%) by treatment of the amino acid *tert*-butyl ester with the corresponding Z-protected amino acid with activation with DCC and DMAP. The obtained fully and orthogonally protected dipeptide was selectively and quantitatively deprotected by catalytic hydrogenation, to afford the *C*-protected compound as a building block for the next elongation step. Finally, peptides containing a GABA$_x$-Gly$_y$ (x = 0–2, y = 0–3) moiety underwent DCC/DMAP-mediated coupling with Fp-GABA-OH (**1**) to provide *C*-protected fulleropeptides in satisfactory yields (57–66%).

The target fulleropeptides **2**, **3**, **5**, **6** and **8**–**12** were obtained by the pathway shown in Scheme 1. The *C*-protected homo-peptides H-(Gly)$_2$-O*t*Bu (**15**) and H-(Gly)$_3$-O*t*Bu (**17**) were prepared from glycine (**13**) and subsequently coupled with fulleropyrrolidinic acid **1** to afford fulleropeptides Fp-GABA-Gly$_2$-O*t*Bu (**5**) and Fp-GABA-Gly$_3$-O*t*Bu (**6**), respectively. Dipeptide **15** was transformed into hetero-tripeptide H-GABA-(Gly)$_2$-O*t*Bu (**19**) by use of Z-GABA (**26**) in a further chain elongation process and then into tetrapeptide H-(GABA)$_2$-(Gly)$_2$-O*t*Bu (**21**, via fully protected compounds **18** and **20**, respectively). In the final steps, the obtained peptides were coupled with GABA-containing fulleropyrolidinic acid **1** (Fp-GABA-OH) by a standard DCC/DMAP procedure to give the two remaining Gly$_2$-containing fulleropeptides **8** and **11** (**19** → **8** and **21**→ **11**).

Analogously, the first coupling cycle of homo-tripeptide H-(Gly)$_3$-O*t*Bu (**17**) and Z-GABA (**26**) gave fully protected tetrapeptide **22**, which after benzyl group removal afforded hetero-tetrapetide **23**. The second coupling cycle led to the formation of hetero-pentapeptide **25** (via fully protected compound **24**). After coupling with Fp-GABA-OH (**1**), the



i) DCC, DMAP, DCM, Ar, r.t., 24 h; ii) Pd-C, MeOH, r.t., 2 h; iii) $BrCH_2CO_2Bn$, TEA, DCM, 0°C to r.t., 24 h; iv) C_{60}, HCHO, PhMe, reflux 4 h (a), 12 h (b)

Scheme 1. Synthesis of fulleropeptides **2**–**12**.

two remaining Gly_3-containing fulleropeptides **9** and **12** were obtained (**23** → **9** and **25** → **12**).

For the preparation of the all-GABA-containing fulleropeptides, Z-GABA (**26**) was transformed into *tert*-butyl 4-aminobutanoate (**27**),[15] which was subsequently coupled with fulleroacid **1** to give fulleropeptide Fp-$GABA_2$-O*t*Bu (**2**). DCC/DMAP-assisted coupling of Z-GABA (**26**) and H-GABA-O*t*Bu (**27**), followed by catalytic hydrogenolysis and coupling with Fp-GABA-OH (**1**), gave fulleropeptide Fp-$GABA_3$-O*t*Bu (**3**).

The simplest fully protected hetero-dipeptide was prepared by employing Z-GABA (**26**) and H-Gly-O*t*Bu as starting materials and subsequently transformed into H-GABA-Gly-O*t*Bu (**31**). A second DCC/DMAP-mediated

cycle with Z-GABA (**26**), followed by catalytic hydrogenolysis, led to tripeptide H-(GABA)$_2$-Gly-O*t*Bu (**33**), which after coupling with fulleroacid **1** afforded fulleropeptide Fp-GABA$_3$-Gly-O*t*Bu (**10**).

[3+2] Cycloadditions of Azomethine Ylides to C_{60}

Although the GABA-containing fulleropyrrolidinic acid Fp-GABA-OH (**1**) was successfully incorporated into nine new fulleropyrrolidinic peptides (and previously also into fullerosteroidal esters[15]), attempted amidation either with H-Gly-O*t*Bu or with H-GABA-Gly-O*t*Bu by the standard DCC/DMAP procedure failed. On the other hand, both amino compounds had successfully been employed as building blocks elsewhere in the peptide elongation process. To overcome the problem and to complete the set of target compounds, another synthetic approach based on [3+2] cycloadditions of azomethine ylides to C_{60} was attempted (Scheme 1). Intermediates **31** and **33**, previously prepared during the synthesis of the fulleropeptide **10**, were used for the formation of peptidic azomethine ylides. Mono-*N*-alkylation of the simplest hetero-dipeptide H-GABA-Gly-O*t*Bu (**31**) with benzyl bromoacetate and subsequent carboxylic group deprotection afforded the glycino derivative **35**. Further condensation with formaldehyde and in situ thermal decarboxylation provided the corresponding peptidic azomethine ylide, which smoothly underwent [3+2] cycloaddition to C_{60} to give fulleropeptide **4** (Fp-GABA-Gly-O*t*Bu). The previously prepared tripeptide H-(GABA)$_2$-Gly-O*t*Bu (**33**) was analogously transformed into the amino acid **37** and subsequently into target fulleropeptide **7** (Fp-GABA$_2$-Gly-O*t*Bu, Scheme 1).

Structure Elucidation

All target compounds gave correct ESI MS spectra with regard to their chemical structures. Their IR spectra each showed strong absorptions at 3228–3311, 1720–1742 and 1641–1653 cm^{-1} attributable to the amide NH, the ester CO and the amide CO stretching bands, respectively. All compounds displayed almost identical absorption behaviour in the UV/Vis range: characteristic absorption bands attributable to the fullerene moiety were observed in the 254–260 nm range, whereas peaks belonging to the amide region appeared in the 303–306 and 319–325 nm ranges. In addition, a weak sharp peak at 430 nm, typical of fulleropyrrolidines,[40] was observed in each spectrum. Because of the potential for incorporation of the synthesized fulleropeptides into more complex structures, such as self-assembled supramolecular aggregates or nanomolecular machines, complete and unambiguous assignments of all spin-active nuclei were made. This was achieved by extensive NMR analysis, involving ^{1}H NMR assignments with the aid of COSY and TOCSY spectra, correlation through $^1J_{C,H}$ values to provide the ^{13}C NMR assignments for protonated carbons and correlation through $^2J_{C,H}$ and $^3J_{C,H}$ values to assign quaternary carbons. This process also provided independent verification of ^{1}H and ^{13}C NMR assignments made with the other methods.

NMR Spectroscopy

All fullero compounds gave the expected ^{1}H NMR spectra, with mainly broad triplets in the downfield region (δ = 6.15–7.99 ppm) attributable to amide protons, a pyrrolidinic strong singlet at δ = 4.4 ppm and doublets or triplets in a very narrow range of δ = 3.91–4.04 ppm ($\Delta\delta_H$ = 0.13 ppm) belonging to glycyl CH_2 groups. The three remaining GABA methylene groups gave the corresponding multiplets at ca. 3.2, 2.5 and 2 ppm (*N*-adjacent, internal, and CH_2 groups next to carbonyl, respectively), whereas the *tert*-butyl signal appeared as strong singlet at δ = 1.44–1.48 ppm.

In the ^{13}C NMR spectra, all peaks, both those belonging to fulleropyrrolidinic carbons and those belonging to the peptide chains, were observed. The C_{2v}-symmetric fulleropeptides each exhibited 16 well-resolved lines for 58 sp^2 fullerene C atoms in the aromatic region (δ = 136–155 ppm), which is in accordance with previously obtained results for GABA-containing fulleropyrrolidinic esters.[15] The two remaining fullerene C atoms (sp^3 C^f-1 and C^f-9; see Figure 2, e) each resonate in the aliphatic region (δ = 70.44–70.83 ppm), together with the pyrrolidinic CH_2 carbons (δ = 67.55–67.95 ppm). The most strongly downfield-shifted aromatic signal (δ = 154.73–155.14 ppm) was assigned to fullerene carbons adjacent to the functionalized 6,6-bond (C^f-2, C^f-5, C^f-8 and C^f-10; see Figure 2, e), because its $^3J_{C,H}$ correlation with the pyrrolidinic signal at 4.4 ppm was observed in the HMBC spectra of all compounds studied (Figure 2, a, d, e). The ^{13}C NMR chemical shifts of the remaining 54 fullerene carbons were consistent with fulleropyrrolidine model compound data.[41]

Assignments of individual resonances belonging to amino acid spin systems were carried out by comparative analysis of COSY and TOCSY spectra. Starting from the N*H* peaks in the downfield region of 6.15–7.99 ppm, correlations with signals at δ = 3.91–4.04 ppm (doublets or triplets, $\Delta\delta_H$ = 0.13) were observed, thus establishing their glycyl C*H*$_2$ origins. The GABA protons were established from TOCSY cross-peaks between amide N*H* at 6.15–7.33 ppm and triplets at δ = 2.25–2.62 [H-C(2), $\Delta\delta_H$ = 0.37], quints at δ = 1.81–2.29 [H-C(3), $\Delta\delta_H$ = 0.48] and triplets or quints at δ 3.13–3.42 ppm [H-C(4), $\Delta\delta_H$ = 0.29]. The ^{13}C NMR chemical shifts of the peptidic moieties in all synthesized compounds also appeared in a very narrow range, thus indicating that the obtained fulleropeptides could be useful as a good model system for further structure determination of more complex systems. A comparative analysis of spectroscopic data obtained from different NMR experiments afforded the following assignments: glycyl methylene signals appeared in the 41.70–43.22 region ($\Delta\delta_c$ = 1.52), and those belonging to GABA–C(2) and C(3) at 33.15–34.65 ($\Delta\delta_c$ = 1.50) and 24.13–26.15 ppm ($\Delta\delta_c$ = 2.02), respectively. The appearance of GABA–C(4) peaks in a significantly wider

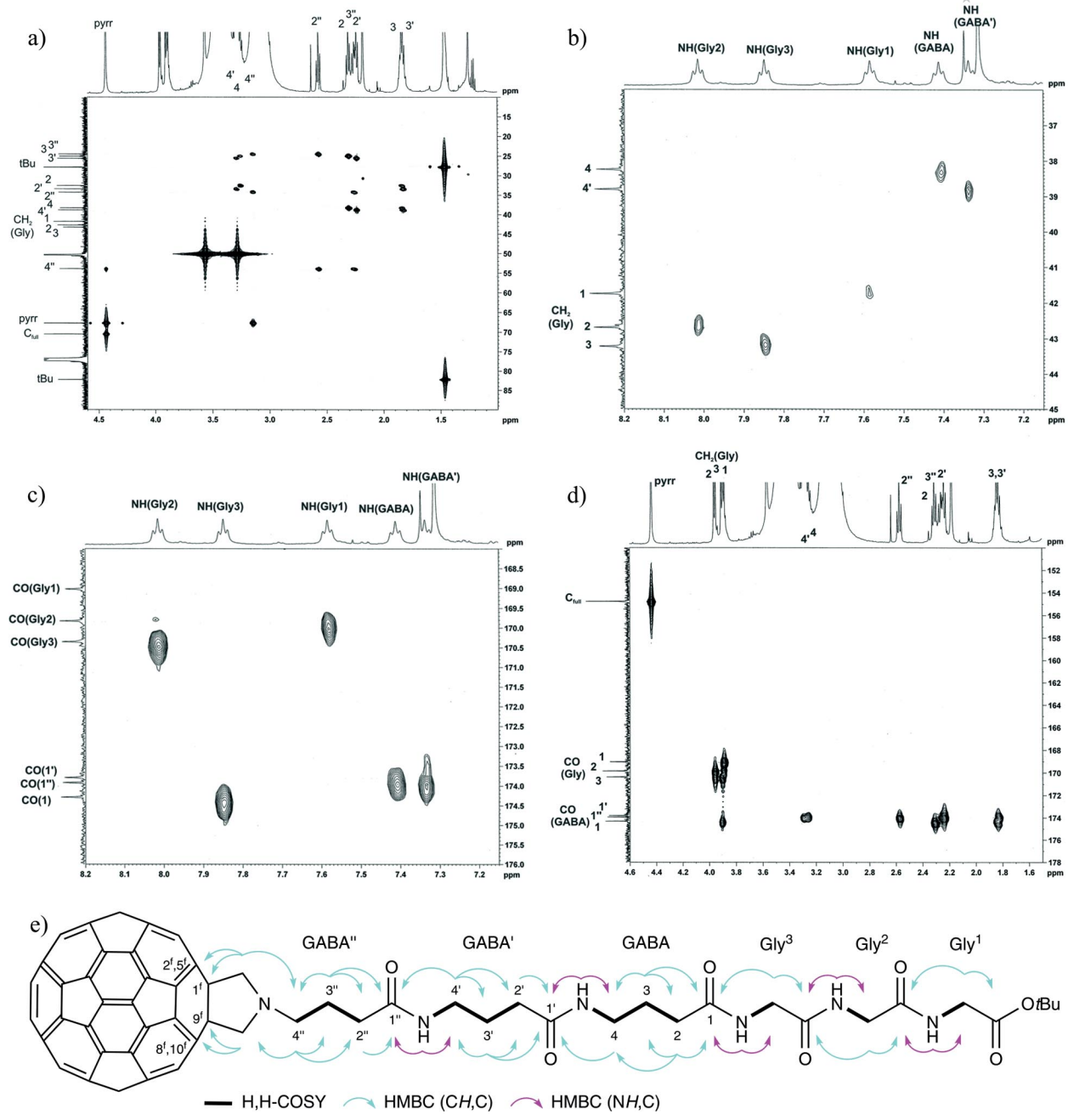


Figure 2. Expanded parts of HMBC spectra of compound **12** showing ^2J and ^3J connectivities in a) the aliphatic *H*/C, b) the amide N*H*/aliphatic C, c) the amide N*H*/CO, and d) the aliphatic *H*/CO regions. e) H,H-COSY and heteronuclear multiple bond correlations in **12**.

range (38.24–53.93 ppm, $\Delta\delta_c$ = 15.69) than GABA–C(2) and C(3) was the consequence of the pyrrolidine ring proximity in compounds **4**–**6**. Detailed regio-comparison of chemical shifts showed that GABA–C(4) also resonated in a quite restricted field range: carbons adjacent to the pyrrolidine ring at 53.24–53.89 ppm ($\Delta\delta_c$ = 0.65), those forming amide moieties at 38.24–39.46 ppm ($\Delta\delta_c$ = 1.22). Their different chemical shifts indicate that the influence of the fulleropyrrolidine fragment on the magnetic environment of the adjacent GABA CH_2 groups is significant. All carbonyl carbons resonated in the expected downfield domain: glycyl at 168.71–170.35, GABA at 172.60–174.36 and ester at 172.60–174.29 ppm. The remaining ester carbons (*t*Bu group) gave the anticipated response at δ = 27.76–28.31 and δ = 80.57–82.48 ppm (CH_3 and C, respectively). The attribution of the GABA residue next to the pyrrolidine ring in each fulleropeptide was made on the basis of the ^{1}H peak multiplicity of the γ methylene protons (triplet) and its HMBC connectivity with the pyrrolidine methylene carbon and provided a starting point for simultaneous assignment of the remaining ^{1}H and ^{13}C NMR resonances in a stepwise manner. Sequential assignment required correlation across the amide bonds separating two proton spin systems of adjacent amino acids. Differentiation of Gly and GABA

amide carbonyl carbons was based on their HMBC correlations. As shown for the example of Fp-hexapeptide *t*Bu ester **12** (Figure 2), each carbonyl group is coupled to three (Gly) or four (GABA) kinds of protons. In the former case these are: 1) the α- and β-protons of its own residue [CO-(Gly)/CH_2(Gly); CO(1)/CH_2 (2,3), Figure 2, d], 2) the neighbouring residue CH_2 protons [CO(Gly^2)/CH_2(Gly^1), CO(Gly^3)/CH_2(Gly^2); CO(1)/CH_2(Gly^3); CO(1′)/CH_2(4); CO(1′′)/CH_2(4′) Figure 2, d], and 3) the amide N*H* protons through two bonds [CO(Gly^2)/N*H*(Gly^1); CO(Gly^3)/N*H*(Gly^2); CO(1)/N*H*(Gly^3); CO(1′)/N*H*(GABA), CO(1′′)/N*H*(GABA′); Figure 2, c]. Also, the HMBC correlations of the amide N*H* protons via $^2J_{C,H}$ with the methylene protons are characteristic for all residues [N*H*(Gly^2)/CH_2(Gly^2); N*H*(Gly^3) /CH_2(Gly^3); N*H*(Gly^1)/CH_2(Gly^1); N*H*(GABA)/CH_2(4); N*H*(GABA′)/CH_2(4′); Figure 2, b]. Together, the observed cross-correlated peaks allowed the attribution of the carbonyl groups (Figure 2, e) and unequivocally validated the assigned structure. The ^{1}H and ^{13}C NMR chemical shift assignments for peptide moieties of fulleropeptides **2**–**12** are given in the Experimental Section. For a table containing these data and additional spectra see the Supporting Information.

Solubility

All of the obtained fulleropeptides are quite soluble in moderately polar media (15 mg mL^{-1} in DCM/MeOH/CS_2 1:1:1, PhMe/DCM/MeOH 1:1:1 and toluene/MeOH 5:1). Compounds **2** and **3**, containing only GABA side chains, and those incorporating GABA$_n$-Gly moieties (n = 1–3; **4**, **7** and **10**, respectively) also reached the same level of solubility in the chlorinated hydrocarbons, whereas the other synthesized fulleropeptides are moderately soluble even in a more polar medium (5 mg mL^{-1} in DCM/MeOH 1:1).

Conclusions

We have designed and synthesized two sets of new fulleropyrrolidines containing repeating GABA and GABA$_n$-Gly$_m$ (n, m = 1–3) units. Most of the target compounds (nine out of 11) were successfully prepared by DCC/DMAP-supported amidation of a previously synthesized GABA-containing fulleropyrrolidinic acid [Fp-GABA-OH (**1**)] with the appropriate *C*-protected small peptides. Attempts to use H-Gly-O*t*Bu and H-GABA-Gly-O*t*Bu as a building blocks in the above process did not provide the expected fulleropeptides, so the two remaining compounds were obtained by different synthetic approach involving [3+2] cycloadditions of azomethine ylides to C_{60} as the key steps. The presented NMR analysis shows that the assignment of peptide spin system can be achieved easily and unequivocally by complementary use of standard 2D NMR experiments (H,H-COSY, HMBC, HSQC, TOCSY). The spin-active nuclei of all synthesized compounds resonate in very narrow ranges, suggesting that the obtained fulleropeptides represent a good model system for further more complex systems. In addition, the highly uniform chemical shifts also represent a powerful tool for an accurate monitoring of their supramolecular organization. Finally, the solubilities of the synthesized compounds are significantly improved relative to C_{60}.

Experimental Section

Abbreviations: DCC = dicyclohexylcarbodiimide, DMAP = 4-(dimethylamino)pyridine, TEA = triethylamine, DCM = dichloromethane.

General: Flash column chromatography (FCC) and TLC were carried out with Merck silica gel (0.04–0.063 mm) and precoated silica gel 60 F_{254} plates, respectively. Melting points were determined with a Boetius PMHK apparatus and were uncorrected. IR spectra (ATR) were recorded with a Perkin–Elmer-FT-IR 1725X spectrophotometer; $\tilde{\nu}$ values are given in cm^{-1}. ^{1}H and ^{13}C NMR spectra were recorded with Varian Gemini 200 and Bruker Avance spectrometers (at 200/500 and 50/125 MHz, respectively). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz. The homonuclear 2D spectra (DQF-COSY, TOCSY) and the heteronuclear 2D ^{1}H-^{13}C spectra (HSQC, HMBC) were recorded with the usual settings. Samples were dissolved in the indicated solvent systems, and TMS was used as internal reference. UV spectra were recorded with a GBC-Cintra 40 UV/Vis spectrophotometer. The high-resolution MS spectra were taken with an Agilent 6210 LC ESI-MS TOF spectrometer. Fulleropyrrolidinic acid **1** (Fp-GABA-OH), *N*-benzyloxycarbonyl-γ-aminobutyric acid (Z-GABA-OH, **26**) and *tert*-butyl 4-aminobutanoate (H-GABA-O*t*Bu, **27**) were synthesized by the published procedures.[15] Yields of the azomethine ylide cycloaddition reactions are reported as absolute values without recovery of the starting fullerene (30–40%) taken into account. Fullerenic carbons, presented as C_f, were numbered in a simplified way, as described in the literature.[25] The amino acids incorporated into peptidic backbones, presented as G, G′ and G′′ (GABA) and Gly^1, Gly^2 and Gly^3, were labelled and numbered in the order of priority (starting from C terminus). For clarity, formulas with individually presented components of peptides are also given in parentheses.

General Procedures

A) DCC/DMAP-Assisted Amidation: DCC (0.10 mmol) was added to a solution of fulleropyrrolidinic acid **1** (Fp-GABA-OH, 85 mg, 0.10 mmol), amine (0.10 mmol) and DMAP (0.01 mmol) in dry DCM (200 mL) and the reaction mixture was stirred at room temperature under Ar for 24 h. Insoluble material (dicyclohexylurea, DCU) was filtered off. In cases of fulleroamide preparations, the solvent was removed under vacuum and the reaction mixture was purified by FCC on SiO_2 with use of the solvents listed below as eluents. Subsequent precipitation from CH_2Cl_2/MeOH/CS_2 solution with MeOH gave pure fulleropeptides.

B) [3+2] Cycloadditions of Azomethine Ylides to C_{60}: A suspension of C_{60} (200 mg, 0.28 mmol), the corresponding amino acid (0.28 mmol) and paraformaldehyde (42 mg, 1.40 mmol, 5 mol equiv.) in PhMe (250 mL) was heated at reflux and the solvent was then evaporated to dryness. The residue was purified by FCC on SiO_2 with use of the gradients of solvents listed below as eluents. The first fraction was unconsumed C_{60} and the second the monoadduct (fulleropeptide **4** or **7**). Subsequent precipitation from CH_2Cl_2/MeOH/CS_2 solution with MeOH gave the pure fulleropeptide.

Fulleropeptide 2 (Fp-GABA$_2$-O*t*Bu, Fp-G′-G-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 100 mg, 0.12 mmol), H-GABA-O*t*Bu (**27**, 20 mg, 0.12 mmol), DMAP (1.5 mg, 0.012 mmol) and DCC (25 mg, 0.12 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc 1:1 gave fulleropeptide **2** (71 mg, 61%). R_f = 0.73 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 6.15 (br. s, 1 H, NH^{GABA}), 4.42 (s, 4 H, $CH_2^{pyrr.}$), 3.37 (q, J = 6.5 Hz, 2 H, CH_2^4), 3.15 (t, J = 7.0 Hz, 2 H, $CH_2^{4'}$), 2.58 (t, J = 7.0 Hz, 2 H, $CH_2^{2'}$), 2.32 (t, J = 7.0 Hz, 4 H, CH_2^2), 2.28 (quint, J = 7.0 Hz, 2 H, $CH_2^{3'}$), 1.85 (quint, J = 7.0 Hz, 2 H, CH_2^3), 1.45 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ = 172.76 (CO^{GABA}), 172.65 ($CO^{GABA'}$), 154.92 (C_f-2, 5, 8, 10), 147.30 (C_f-52, 60), 146.24 (C_f-32, 39, 41, 48), 146.06 (C_f-3, 4, 25, 26), 146.02 (C_f-51, 53, 56, 59), 145.64 (C_f-21, 30), 145.42 (C_f-14, 19, 23, 28), 145.28 (C_f-49, 50, 54, 55), 144.54 (C_f-33, 38, 42, 47), 143.09 (C_f-31, 40), 142.63 (C_f-35, 36, 57, 58), 142.21 (C_f-13, 20, 22, 29), 142.05 (C_f-34, 37, 43, 46), 141.88 (C_f-16, 17, 44, 45), 140.18 (C_f-15, 18, 24, 27), 136.10 (C_f-6, 7, 11, 12), 80.57 (C^{tBu}), 70.60 (C_f-1, 9), 67.69 ($CH_2^{pyrr.}$), 53.54 ($CH_2^{4'}$), 39.24 (CH_2^4), 34.32 ($CH_2^{2'}$), 33.15 (CH_2^2), 28.09 (CH_3^{tBu}), 24.84 (CH_2^3), 24.36 ($CH_2^{3'}$) ppm. IR: $\tilde{\nu}$ = 3311, 2970, 2923, 2805, 2739, 1720, 1644, 1533, 1427, 1362, 1339, 1225, 1149 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3900), 323 (39000), 305 (40000), 255 nm (98000 mol^{-1} dm cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{74}H_{27}N_2O_3$ 991.20162 $[M + H]^+$; found 991.20145.

Fulleropeptide 3 (Fp-GABA$_3$-O*t*Bu, Fp-G′′-G′-G-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 100 mg, 0.12 mmol), H-(GABA)$_2$-O*t*Bu (**29**, 29 mg, 0.12 mmol), DMAP (1.5 mg, 0.012 mmol) and DCC (25 mg, 0.12 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:0.5 gave fulleropeptide **3** (84 mg, 66%). R_f = 0.54 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 6.56 (br. t, J = 5.5 Hz, 1 H, $NH^{GABA'}$), 6.38 (br. s, 1 H, NH^{GABA}), 4.42 (s, 4 H, $CH_2^{pyrr.}$), 3.38 (q, J = 6.0 Hz, 2 H, $CH_2^{4'}$), 3.29 (q, J = 7.0 Hz, 2 H, CH_2^4), 3.16 (t, J = 6.5 Hz, 2 H, $CH_2^{4''}$), 2.60 (t, J = 7.2 Hz, 2 H, $CH_2^{2''}$), 2.28 (m, 6 H, $CH_2^{2,2',3''}$), 1.87 (quint, J = 7.0 Hz, 2 H, $CH_2^{3'}$), 1.81 (quint, J = 7.0 Hz, 2 H, CH_2^3), 1.44 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ = 173.42 ($CO^{GABA''}$), 172.98 (CO^{GABA}), 172.92 ($CO^{GABA'}$), 155.14 (C_f-2, 5, 8, 10), 147.53 (C_f-52, 60), 146.47 (C_f-32, 39, 41, 48), 146.29 (C_f-3, 4, 25, 26), 146.24 (C_f-51, 53, 56, 59), 145.86 (C_f-21, 30), 145.65 (C_f-14, 19, 23, 28), 145.51 (C_f-49, 50, 54, 55), 144.77 (C_f-33, 38, 42, 47), 143.32 (C_f-31, 40), 142.86 (C_f-35, 36, 57, 58), 142.43 (C_f-13, 20, 22, 29), 142.28 (C_f-34, 37, 43, 46), 142.11 (C_f-16, 17, 44, 45), 140.41 (C_f-15, 18, 24, 27), 136.33 (C_f-6, 7, 11, 12), 80.78 (C^{tBu}), 70.83 (C_f-1, 9), 67.95 ($CH_2^{pyrr.}$), 53.89 ($CH_2^{4''}$), 39.46 (CH_2^4), 39.44 ($CH_2^{4'}$), 34.65 ($CH_2^{2''}$), 34.29 ($CH_2^{2'}$), 33.34 (CH_2^2), 28.31 (CH_3^{tBu}), 25.91 ($CH_2^{3'}$), 24.90 (CH_2^3), 24.64 ($CH_2^{3''}$) ppm. IR: $\tilde{\nu}$ = 3292, 3081, 2929, 2869, 2788, 1723, 1641, 1546, 1430, 1365, 1257, 1153 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3900), 322 (37000), 304 (38000), 257 nm (114000 mol^{-1} dm^3 cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{78}H_{34}N_3O_4$ 1076.25438 $[M + H]^+$; found 1076.25621.

Fulleropeptide 4 (Fp-GABA-Gly-O*t*Bu, Procedure B): A suspension of C_{60} (200 mg, 0.28 mmol), amino acid **35** (76 mg, 0.28 mmol) and paraformaldehyde (42 mg, 1.40 mmol, 5 mol equiv.) in toluene (250 mL) was heated at reflux for 4 h. Elution with PhMe gave unreacted C_{60} (130 mg, 65%), and elution with PhMe/EtOAc 6:4 afforded fulleropeptide **4** (69 mg, 26%). R_f = 0.83 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 6.54 (br. s, 1 H, NH^{Gly}), 4.45 (s, 4 H, $CH_2^{pyrr.}$), 4.02 (d, J = 5.0 Hz, 2 H, CH_2^{Gly}), 3.20 (t, J = 6.8 Hz, 2 H, CH_2^4), 2.68 (t, J = 6.8 Hz, 2 H, CH_2^2), 2.30 (quint, J = 6.9 Hz, 2 H, CH_2^3), 1.47 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2$): δ = 172.60 (CO^{GABA}), 169.18 (CO^{Gly}), 154.90 (C_f-2, 5, 8, 10), 147.24 (C_f-52, 60), 146.19 (C_f-32, 39, 41, 48, 3, 4, 25, 26), 146.00 (C_f-51, 53, 56, 59), 145.61 (C_f-21, 30), 145.36 (C_f-14, 19, 23, 28), 145.23 (C_f-49, 50, 54, 55), 144.50 (C_f-33, 38, 42, 47), 143.03 (C_f-31, 40), 142.57 (C_f-35, 36, 57, 58), 142.19 (C_f-13, 20, 22, 29), 142.01 (C_f-34, 37, 43, 46), 141.83 (C_f-16, 17, 44, 45), 140.12 (C_f-15, 18, 24, 27), 136.06 (C_f-6, 7, 11, 12), 82.11 (C^{tBu}), 70.56 (C_f-1, 9), 67.55 ($CH_2^{pyrr.}$), 53.24 (CH_2^4), 42.07 (CH_2^{Gly}), 33.94 (CH_2^2), 28.00 (CH_3^{tBu}), 24.17 (CH_2^3) ppm. IR: $\tilde{\nu}$ = 3303, 2972, 2796, 1739, 1653, 1536, 1508, 1366, 1222, 1154, 1034 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (1700), 325 (17000), 303 (17000), 256 nm (55000 mol^{-1} dm^3 cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{72}H_{23}N_2O_3$ 963.17032 $[M + H]^+$; found 963.17012.

Fulleropeptide 5 (Fp-GABA-Gly$_2$-O*t*Bu, Fp-G-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-(Gly)$_2$-O*t*Bu (**15**, 18 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:0.5 gave fulleropeptide **5** (63 mg, 65%). R_f = 0.61 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 7.08 (br. t, J = 4.5 Hz, 1 H, NH^{Gly2}), 6.83 (br. s, 1 H, NH^{Gly1}), 4.44 (s, 4 H, $CH_2^{pyrr.}$), 4.04 (d, J = 5.5 Hz, 2 H, CH_2^{Gly2}), 3.93 (d, J = 5.0 Hz, 2 H, CH_2^{Gly1}), 3.19 (t, J = 7.0 Hz, 2 H, CH_2^4), 2.68 (t, J = 7.5 Hz, 2 H, CH_2^2), 2.30 (quint, J = 7.0 Hz, 2 H, CH_2^3), 1.47 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 173.55 (CO^{GABA}), 169.09 (CO^{Gly2}), 168.71 (CO^{Gly1}), 154.88 (C_f-2, 5, 8, 10), 147.26 (C_f-52, 60), 146.20 (C_f-32, 39, 41, 48), 146.02 (C_f-3, 4, 25, 26), 145.99 (C_f-51, 53, 56, 59), 145.61 (C_f-21, 30), 145.37 (C_f-14, 19, 23, 28), 145.24 (C_f-49, 50, 54, 55), 144.50 (C_f-33, 38, 42, 47), 143.04 (C_f-31, 40), 142.59 (C_f-35, 36, 57, 58), 142.18 (C_f-13, 20, 22, 29), 142.02 (C_f-34, 37, 43, 46), 141.84 (C_f-16, 17, 44, 45), 140.13 (C_f-15, 18, 24, 27), 136.06 (C_f-6, 7, 11, 12), 82.48 (C^{tBu}), 70.57 (C_f-1, 9), 67.67 ($CH_2^{pyrr.}$), 53.63 (CH_2^4), 43.00 (CH_2^{Gly2}), 41.96 (CH_2^{Gly1}), 34.03 (CH_2^2), 27.95 (CH_3^{tBu}), 24.19 (CH_2^3) ppm. IR: $\tilde{\nu}$ = 3294, 2970, 2928, 2782, 1736, 1652, 1512, 1426, 1365, 1223, 1153, 1116, 1031 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3600), 321 (36000), 305 (37000), 254 nm (100000 mol^{-1} dm^3 cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{74}H_{26}N_3O_4$ 1020.19178 $[M + H]^+$; found 1020.19096.

Fulleropeptide 6 (Fp-GABA-Gly$_3$-O*t*Bu, Fp-G-Gly^3-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-(Gly)$_3$-O*t*Bu (**17**, 23 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:0.3 gave fulleropeptide **6** (65 mg, 64%). R_f = 0.51 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2$): δ = 7.02 (br. s, 1 H, NH^{Gly3}), 6.96 (br. s, 1 H, NH^{Gly2}), 6.64 (br. s, 1 H, NH^{Gly1}), 4.43 (s, 4 H, $CH_2^{pyrr.}$), 4.03 (d, J = 5.0 Hz, 2 H, CH_2^{Gly3}), 3.99 (d, J = 5.0 Hz, 2 H, CH_2^{Gly2}), 3.92 (d, J = 5.0 Hz, 2 H, CH_2^{Gly1}), 3.18 (t, J = 6.0 Hz, 2 H, CH_2^4), 2.69 (t, J = 7.0 Hz, 2 H, CH_2^2), 2.28 (quint, J = 7.0 Hz, 2 H, CH_2^3), 1.46 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 174.36 (CO^{GABA}), 170.03 (CO^{Gly3}), 169.55 (CO^{Gly1}), 169.13 (CO^{Gly2}), 154.73 (C_f-2, 5, 8, 10), 147.14 (C_f-52, 60), 146.08 (C_f-32, 39, 41, 48), 145.91 (C_f-3, 4, 25, 26), 145.85 (C_f-51, 53, 56, 59), 145.49 (C_f-21, 30), 145.26 (C_f-14, 19, 23, 28), 145.12 (C_f-49, 50, 54, 55), 144.38 (C_f-33, 38, 42, 47), 142.94 (C_f-31, 40), 142.48 (C_f-35, 36, 57, 58), 142.04 (C_f-13, 20, 22, 29), 141.90 (C_f-34, 37, 43, 46), 141.73 (C_f-16, 17, 44, 45), 140.02 (C_f-15, 18, 24, 27), 135.96 (C_f-6, 7, 11, 12), 82.28 (C^{tBu}), 70.44 (C_f-1, 9), 67.61 ($CH_2^{pyrr.}$), 53.74 (CH_2^4), 42.97 (CH_2^{Gly3}), 42.51 (CH_2^{Gly2}), 41.70 (CH_2^{Gly1}), 33.74 (CH_2^2), 27.76 (CH_3^{tBu}), 24.13 (CH_2^3) ppm. IR: $\tilde{\nu}$ = 3288, 2928, 2782, 1736, 1653, 1532, 1425, 1367, 1226, 1156, 1024 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3000), 321 (29000),

304 (30000), 255 nm (94000 $mol^{-1}\,dm^3\,cm^{-1}$). ESI-TOF-MS: *m/z* = calcd. for $C_{76}H_{29}N_4O_5$ 1077.21325 $[M + H]^+$; found 1077.21443.

Fulleropeptide 7 (Fp-GABA$_2$-Gly-O*t*Bu, Fp-G′-G-Gly-O*t*Bu, Procedure B): A suspension of C_{60} (200 mg, 0.28 mmol), amino acid **37** (101 mg, 0.28 mmol) and paraformaldehyde (42 mg, 1.40 mmol, 5 mol equiv.) in PhMe (250 mL) was heated at reflux for 12 h and the solvents were evaporated to dryness. Elution with PhMe gave unreacted C_{60} (87 mg, 44%) and elution with PhMe/EtOAc/MeOH 5:5:0.1 provided fulleropeptide **7** (44 mg, 15%). R_f = 0.48 ($C_6H_5CH_3$/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3$/CS_2): δ = 6.53 (br. s, 1 H, NH^{Gly}), 6.49 (br. s, 1 H, NH^{GABA}), 4.42 (s, 4 H, $CH_2^{pyrr.}$), 3.94 (d, *J* = 5.0 Hz, 2 H, CH_2^{Gly}), 3.42 (q, *J* = 6.0 Hz, 2 H, CH_2^{4}), 3.15 (t, *J* = 7.0 Hz, 2 H, $CH_2^{4'}$), 2.60 (t, *J* = 7.0 Hz, 2 H, $CH_2^{2'}$), 2.34 (t, *J* = 7.0 Hz, 2 H, CH_2^{2}), 2.28 (quint, *J* = 7.0 Hz, 2 H, $CH_2^{3'}$), 1.90 (quint, *J* = 6.5 Hz, 2 H, CH_2^{3}), 1.47 (s, 9 H, $CH_3^{t\mathrm{Bu}}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/CS_2): δ = 173.40 ($CO^{GABA'}$), 172.91 (CO^{GABA}), 169.28 (CO^{Gly}), 155.13 (C_f-2, 5, 8, 10), 147.52 (C_f-52, 60), 146.47 (C_f-32, 39, 41, 48), 146.29 (C_f-3, 4, 25, 26), 146.24 (C_f-51, 53, 56, 59), 145.86 (C_f-21, 30), 145.64 (C_f-14, 19, 23, 28), 145.50 (C_f-49, 50, 54, 55), 144.76 (C_f-33, 38, 42, 47), 143.31 (C_f-31, 40), 142.85 (C_f-35, 36, 57, 58), 142.43 (C_f-13, 20, 22, 29), 142.27 (C_f-34, 37, 43, 46), 142.10 (C_f-16, 17, 44, 45), 140.40 (C_f-15, 18, 24, 27), 136.33 (C_f-6, 7, 11, 12), 82.43 ($C^{t\mathrm{Bu}}$), 70.83 (C_f-1, 9), 67.94 ($CH_2^{pyrr.}$), 53.86 ($CH_2^{4'}$), 42.31 (CH_2^{Gly}), 39.30 (CH_2^{4}), 34.58 ($CH_2^{2'}$), 33.94 (CH_2^{2}), 28.27 ($CH_3^{t\mathrm{Bu}}$), 25.88 (CH_2^{3}), 24.63 ($CH_2^{3'}$) ppm. IR: $\tilde{\nu}$ = 3297, 3083, 2928, 2795, 1742, 1644, 1543, 1428, 1367, 1224, 1157, 1035 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3400), 321 (32000), 305 (33000), 257 nm (91000 $mol^{-1}\,dm^3\,cm^{-1}$). ESI-TOF-MS: *m/z* = calcd. for $C_{76}H_{30}N_3O_4$ 1048.22308 $[M + H]^+$; found 1048.22599.

Fulleropeptide 8 (Fp-GABA$_2$-Gly$_2$-O*t*Bu, Fp-G′-G-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-GABA-(Gly)$_2$-O*t*Bu (**19**, 26 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:1 gave fulleropeptide **8** (61 mg, 59%). R_f = 0.31 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3$/CS_2/CH_3OH): δ = 7.50 (br. t, *J* = 5.2 Hz, 1 H, NH^{Gly2}), 7.37 (br. t, *J* = 5.0 Hz, 1 H, NH^{Gly1}), 7.10 (br. t, *J* = 5.5 Hz, 1 H, NH^{GABA}), 4.44 (s, 4 H, $CH_2^{pyrr.}$), 3.94 (d, *J* = 5.5 Hz, 2 H, CH_2^{Gly2}), 3.92 (t, *J* = 5.5 Hz, 2 H, CH_2^{Gly1}), 3.34 (q, *J* = 6.5 Hz, 2 H, CH_2^{4}), 3.15 (t, *J* = 7.0 Hz, 2 H, $CH_2^{4'}$), 2.57 (t, *J* = 7.5 Hz, 2 H, $CH_2^{2'}$), 2.33 (t, *J* = 7.0 Hz, 2 H, CH_2^{2}), 2.26 (quint, *J* = 7.0 Hz, 2 H, $CH_2^{3'}$), 1.88 (quint, *J* = 6.7 Hz, 2 H, CH_2^{3}), 1.47 (s, 9 H, $CH_3^{t\mathrm{Bu}}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/CS_2/CH_3OH): δ = 173.82 (CO^{GABA}), 173.73 ($CO^{GABA'}$), 169.62 (CO^{Gly2}), 168.97 (CO^{Gly1}), 154.73 (C_f-2, 5, 8, 10), 147.19 (C_f-52, 60), 146.14 (C_f-32, 39, 41, 48), 145.96 (C_f-3, 4, 25, 26), 145.88 (C_f-51, 53, 56, 59), 145.52 (C_f-21, 30), 145.32 (C_f-14, 19, 23, 28), 145.17 (C_f-49, 50, 54, 55), 144.43 (C_f-33, 38, 42, 47), 142.99 (C_f-31, 40), 142.53 (C_f-35, 36, 57, 58), 142.07 (C_f-13, 20, 22, 29), 141.95 (C_f-34, 37, 43, 46), 141.78 (C_f-16, 17, 44, 45), 140.07 (C_f-15, 18, 24, 27), 136.01 (C_f-6, 7, 11, 12), 82.29 ($C^{t\mathrm{Bu}}$), 70.46 (C_f-1, 9), 67.66 ($CH_2^{pyrr.}$), 53.85 ($CH_2^{4'}$), 42.78 (CH_2^{Gly2}), 41.80 (CH_2^{Gly1}), 38.65 (CH_2^{4}), 34.15 ($CH_2^{2'}$), 33.08 (CH_2^{2}), 27.84 ($CH_3^{t\mathrm{Bu}}$), 25.33 (CH_2^{3}), 24.39 ($CH_2^{3'}$) ppm. IR: $\tilde{\nu}$ = 3299, 3078, 2972, 2928, 2796, 1740, 1650, 1539, 1427, 1368, 1225, 1157, 1032 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3600), 321 (32000), 305 (33000), 260 nm (88000 $mol^{-1}\,dm^3\,cm^{-1}$). ESI-TOF-MS: *m/z* = calcd. for $C_{78}H_{33}N_4O_5$: 1105.24455 $[M + H]^+$; found 1105.24602.

Fulleropeptide 9 (Fp-GABA$_2$-Gly$_3$-O*t*Bu, Fp-G′-G-Gly^3-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-GABA-(Gly)$_3$-O*t*Bu (**23**, 31 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:1.5 gave fulleropeptide **9** (62 mg, 57%). R_f = 0.17 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3$/CS_2/CH_3OH): δ = 7.84 (br. t, *J* = 5.5 Hz, 1 H, NH^{Gly2}), 7.64 (br. t, *J* = 5.2 Hz, 1 H, NH^{Gly3}), 7.38 (br. t, *J* = 5.2 Hz, 1 H, NH^{Gly1}), 7.06 (br. t, *J* = 5.5 Hz, 1 H, NH^{GABA}), 4.43 (s, 4 H, $CH_2^{pyrr.}$), 3.97 (d, *J* = 5.5 Hz, 2 H, CH_2^{Gly2}), 3.91 (t, *J* = 5.8 Hz, 4 H, $CH_2^{Gly1,Gly3}$), 3.34 (q, *J* = 6.5 Hz, 2 H, CH_2^{4}), 3.15 (t, *J* = 7.0 Hz, 2 H, $CH_2^{4'}$), 2.58 (t, *J* = 7.5 Hz, 2 H, $CH_2^{2'}$), 2.34 (t, *J* = 7.0 Hz, 2 H, CH_2^{2}), 2.26 (quint, *J* = 7.0 Hz, 2 H, $CH_2^{3'}$), 1.87 (quint, *J* = 6.5 Hz, 2 H, CH_2^{3}), 1.47 (s, 9 H, $CH_3^{t\mathrm{Bu}}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/CS_2/CH_3OH): δ = 174.25 (CO^{GABA}), 173.92 ($CO^{GABA'}$), 170.16 (CO^{Gly3}), 169.59 (CO^{Gly2}), 169.12 (CO^{Gly1}), 154.74 (C_f-2, 5, 8, 10), 147.22 (C_f-52, 60), 146.16 (C_f-32, 39, 41, 48), 145.98 (C_f-3, 4, 25, 26), 145.89 (C_f-51, 53, 56, 59), 145.53 (C_f-21, 30), 145.34 (C_f-14, 19, 23, 28), 145.20 (C_f-49, 50, 54, 55), 144.45 (C_f-33, 38, 42, 47), 143.01 (C_f-31, 40), 142.56 (C_f-35, 36, 57, 58), 142.09 (C_f-13, 20, 22, 29), 141.97 (C_f-34, 37, 43, 46), 141.80 (C_f-16, 17, 44, 45), 140.10 (C_f-15, 18, 24, 27), 136.00 (C_f-6, 7, 11, 12), 82.29 ($C^{t\mathrm{Bu}}$), 70.48 (C_f-1, 9), 67.69 ($CH_2^{pyrr.}$), 53.81 ($CH_2^{4'}$), 43.20 (CH_2^{Gly3}), 42.66 (CH_2^{Gly2}), 41.76 (CH_2^{Gly1}), 38.55 (CH_2^{4}), 34.21 ($CH_2^{2'}$), 32.86 (CH_2^{2}), 27.85 ($CH_3^{t\mathrm{Bu}}$), 25.45 (CH_2^{3}), 24.40 ($CH_2^{3'}$) ppm. IR: $\tilde{\nu}$ = 3305, 3079, 2930, 2794, 1740, 1648, 1538, 1428, 1390, 1230, 1158, 1031 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (2800), 321 (26000), 305 (27000), 255 nm (86000 $mol^{-1}\,dm^3\,cm^{-1}$). ESI-TOF-MS: *m/z* = calcd. for $C_{80}H_{36}N_5O_6$ 1162.26601 $[M + H]^+$; found 1162.26911.

Fulleropeptide 10 (Fp-GABA$_3$-Gly-O*t*Bu, Fp-G′′-G′-G-Gly-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 73 mg, 0.086 mmol), H-(GABA)$_2$-Gly-O*t*Bu (**33**, 26 mg, 0.086 mmol), DMAP (1 mg, 0.0086 mmol) and DCC (18 mg, 0.086 mmol) in dry DCM (200 mL) were used. Elution with PhMe/EtOAc/MeOH 5:5:0.5 gave fulleropeptide **10** (73 mg, 75%). R_f = 0.46 ($C_6H_5CH_3$/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3$/CS_2): δ = 6.89 (br. t, *J* = 5.5 Hz, 1 H, NH^{GABA}), 6.83 (br. s, 1 H, NH^{Gly}), 6.62 (br. t, *J* = 5.5 Hz, 1 H, $NH^{GABA'}$), 4.42 (s, 4 H, $CH_2^{pyrr.}$), 3.94 (d, *J* = 5.0 Hz, 2 H, CH_2^{Gly}), 3.38 (q, *J* = 6.0 Hz, 2 H, $CH_2^{4'}$), 3.34 (q, *J* = 6.0 Hz, 2 H, CH_2^{4}), 3.16 (t, *J* = 6.5 Hz, 2 H, $CH_2^{4''}$), 2.62 (t, *J* = 7.0 Hz, 2 H, $CH_2^{2''}$), 2.34 (t, *J* = 6.5 Hz, 2 H, CH_2^{2}), 2.27 (t, *J* = 6.5 Hz, 4 H, $CH_2^{3'',2'}$), 1.87 (m, 4 H, $CH_2^{3,3'}$), 1.48 (s, 9 H, $CH_3^{t\mathrm{Bu}}$) ppm. ^{13}C NMR (125 MHz, $CDCl_3$/CS_2): δ = 173.64 ($CO^{GABA''}$), 173.19 ($CO^{GABA'}$), 173.12 (CO^{GABA}), 169.46 (CO^{Gly}), 155.04 (C_f-2, 5, 8, 10), 147.52 (C_f-52, 60), 146.47 (C_f-32, 39, 41, 48), 146.29 (C_f-3, 4, 25, 26), 146.19 (C_f-51, 53, 56, 59), 145.82 (C_f-21, 30), 145.65 (C_f-14, 19, 23, 28), 145.50 (C_f-49, 50, 54, 55), 144.75 (C_f-33, 38, 42, 47), 143.32 (C_f-31, 40), 142.86 (C_f-35, 36, 57, 58), 142.40 (C_f-13, 20, 22, 29), 142.26 (C_f-34, 37, 43, 46), 142.10 (C_f-16, 17, 44, 45), 140.41 (C_f-15, 18, 24, 27), 136.29 (C_f-6, 7, 11, 12), 82.32 ($C^{t\mathrm{Bu}}$), 70.78 (C_f-1, 9), 67.94 ($CH_2^{pyrr.}$), 53.82 ($CH_2^{4''}$), 42.24 (CH_2^{Gly}), 39.24 ($CH_2^{4'}$), 39.11 (CH_2^{4}), 34.63 ($CH_2^{2''}$), 34.04 ($CH_2^{2'}$), 33.79 (CH_2^{2}), 28.26 ($CH_3^{t\mathrm{Bu}}$), 26.15 ($CH_2^{3'}$), 25.52 (CH_2^{3}), 24.59 ($CH_2^{3''}$) ppm. IR: $\tilde{\nu}$ = 3293, 3081, 2925, 2853, 2796, 1742, 1641, 1546, 1456, 1367, 1224, 1157, 1117 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3600), 320 (32000), 306 (34000), 255 nm (96000 $mol^{-1}\,dm^3\,cm^{-1}$). ESI-TOF-MS: *m/z* = calcd. for $C_{80}H_{37}N_4O_5$ 1133.27585 $[M + H]^+$; found 1133.27533.

Fulleropeptide 11 (Fp-GABA$_3$-Gly$_2$-O*t*Bu, Fp-G′′-G′-G-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-(GABA)$_2$-(Gly)$_2$-O*t*Bu (**21**, 34 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with DCM/MeOH 95:5 gave fulleropeptide (**11**, 74 mg, 66%). R_f = 0.27 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3$/CS_2/CH_3OH): δ = 7.57 (br. t, *J* = 5.5 Hz, 1 H,

NH^{Gly2}), 7.40 (br. t, J = 5.0 Hz, 1 H, NH^{Gly1}), 7.33 (br. t, J = 5.5 Hz, 1 H, NH^{GABA}), 7.19 (br. t, J = 5.5 Hz, 1 H, NH$^{GABA'}$), 4.44 (s, 4 H, $CH_2^{pyrr.}$), 3.95 (d, J = 5.5 Hz, 2 H, CH_2^{Gly2}), 3.92 (d, J = 6.0 Hz, 2 H, CH_2^{Gly1}), 3.32 (q, J = 6.5 Hz, 2 H, $CH_2^{4'}$), 3.28 (q, J = 6.0 Hz, 2 H, CH_2^{4}), 3.16 (t, J = 7.0 Hz, 2 H, $CH_2^{4''}$), 2.59 (t, J = 7.5 Hz, 2 H, $CH_2^{2''}$), 2.32 (t, J = 6.5 Hz, 2 H, CH_2^{2}), 2.27 (part of quint, J = 6.5 Hz, 2 H, $CH_2^{3''}$), 2.25 (t, J = 7.0 Hz, 2 H, $CH_2^{2'}$), 1.85 (m, 4 H, $CH_2^{3,3'}$), 1.47 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 173.95 (CO$^{GABA''}$), 173.91 (CO^{GABA}), 173.78 (CO$^{GABA'}$), 169.77 (CO^{Gly2}), 169.00 (CO^{Gly1}), 154.79 (C_f-2, 5, 8, 10), 147.22 (C_f-52, 60), 146.16 (C_f-32, 39, 41, 48), 145.98 (C_f-3, 4, 25, 26), 145.91 (C_f-51, 53, 56, 59), 145.55 (C_f-21, 30), 145.34 (C_f-14, 19, 23, 28), 145.20 (C_f-49, 50, 54, 55), 144.46 (C_f-33, 38, 42, 47), 143.01 (C_f-31, 40), 142.55 (C_f-35, 36, 57, 58), 142.09 (C_f-13, 20, 22, 29), 141.97 (C_f-34, 37, 43, 46), 141.80 (C_f-16, 17, 44, 45), 140.09 (C_f-15, 18, 24, 27), 136.02 (C_f-6, 7, 11, 12), 82.34 (C^{tBu}), 70.50 (C_f-1, 9), 67.69 ($CH_2^{pyrr.}$), 53.87 ($CH_2^{4''}$), 42.81 (CH_2^{Gly2}), 41.84 (CH_2^{Gly1}), 38.87 ($CH_2^{4'}$), 38.53 (CH_2^{4}), 34.25 ($CH_2^{2''}$), 33.51 ($CH_2^{2'}$), 32.96 (CH_2^{2}), 27.86 (CH_3^{tBu}), 25.52 ($CH_2^{3'}$), 25.01 (CH_2^{3}), 24.45 ($CH_2^{3''}$) ppm. IR: $\tilde{\nu}$ = 3296, 3082, 2932, 2795, 1741, 1647, 1544, 1427, 1368, 1225, 1157, 1117, 1031, 846, 772, 527 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (2800), 319 (27000), 305 (28000), 255 nm (88000 mol^{-1} dm^3 cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{82}H_{40}N_5O_6$ 1190.29731 [M + H]$^+$; found 1190.29755.

Fulleropeptide 12 (Fp-GABA$_3$-Gly$_3$-O*t*Bu, Fp-G′′-G′-G-Gly^3-Gly^2-Gly^1-O*t*Bu, Procedure A): Fp-GABA-OH (**1**, 80 mg, 0.094 mmol), H-(GABA)$_2$-(Gly)$_3$-O*t*Bu (**25**, 39 mg, 0.094 mmol), DMAP (1.1 mg, 0.009 mmol) and DCC (19 mg, 0.094 mmol) in dry DCM (200 mL) were used. Elution with DCM/MeOH 85:15 gave fulleropeptide **12** (78 mg, 66%). R_f = 0.12 (PhMe/EtOAc/MeOH 5:5:1). ^{1}H NMR (500 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 7.99 (br. t, J = 5.5 Hz, 1 H, NH^{Gly2}), 7.77 (br. t, J = 5.5 Hz, 1 H, NH^{Gly3}), 7.49 (br. t, J = 5.5 Hz, 1 H, NH^{Gly1}), 7.27 (br. t, J = 6.0 Hz, 1 H, NH^{GABA}), 7.20 (br. t, J = 5.5 Hz, 1 H, NH$^{GABA'}$), 4.43 (s, 4 H, $CH_2^{pyrr.}$), 3.97 (d, J = 6.0 Hz, 2 H, CH_2^{Gly2}), 3.91 (d, J = 6.0 Hz, 2 H, CH_2^{Gly3}), 3.90 (d, J = 5.5 Hz, 2 H, CH_2^{Gly1}), 3.31 (overlapped with MeOH, part of q, 2 H, $CH_2^{4'}$), 3.26 (q, J = 6.0 Hz, 2 H, CH_2^{4}), 3.15 (t, J = 7.0 Hz, 2 H, $CH_2^{4''}$), 2.58 (t, J = 6.0 Hz 2 H, $CH_2^{2''}$), 2.31 (t, J = 6.5 Hz, 2 H, CH_2^{2}), 2.25 (m, 4 H, $CH_2^{2',3''}$), 1.84 (m, 4 H, $CH_2^{3,3'}$), 1.46 (s, 9 H, CH_3^{tBu}) ppm. ^{13}C NMR (125 MHz, $CDCl_3/CS_2/CH_3OH$): δ = 174.29 (CO^{GABA}), 173.92 (CO$^{GABA''}$), 173.79 (CO$^{GABA'}$), 170.35 (CO^{Gly3}), 169.82 (CO^{Gly2}), 169.02 (CO^{Gly1}), 154.74 (C_f-2, 5, 8, 10), 147.20 (C_f-52, 60), 146.15 (C_f-32, 39, 41, 48), 145.98 (C_f-3, 4, 25, 26), 145.88 (C_f-51, 53, 56, 59), 145.52 (C_f-21, 30), 145.33 (C_f-14, 19, 23, 28), 145.19 (C_f-49, 50, 54, 55), 144.44 (C_f-33, 38, 42, 47), 143.01 (C_f-31, 40), 142.55 (C_f-35, 36, 57, 58), 142.08 (C_f-13, 20, 22, 29), 141.95 (C_f-34, 37, 43, 46), 141.79 (C_f-16, 17, 44, 45), 140.09 (C_f-15, 18, 24, 27), 136.00 (C_f-6, 7, 11, 12), 82.18 (C^{tBu}), 70.47 (C_f-1, 9), 67.69 ($CH_2^{pyrr.}$), 53.86 ($CH_2^{4''}$), 43.22 (CH_2^{Gly3}), 42.69 (CH_2^{Gly2}), 41.74 (CH_2^{Gly1}), 38.80 ($CH_2^{4'}$), 38.24 (CH_2^{4}), 34.23 ($CH_2^{2''}$), 33.37 ($CH_2^{2'}$), 32.53 (CH_2^{2}), 27.83 (CH_3^{tBu}), 25.57 ($CH_2^{3'}$), 25.02 (CH_2^{3}), 24.47 ($CH_2^{3''}$) ppm. IR: $\tilde{\nu}$ = 3296, 3082, 2931, 2798, 1738, 1643, 1547, 1426, 1368, 1227, 1157, 1117, 1028 cm^{-1}. UV/Vis ($CHCl_3$): λ_{max} (ε) = 430 (3500), 322 (32000), 306 (34000), 255 nm (103000 mol^{-1} dm^3 cm^{-1}). ESI-TOF-MS: m/z = calcd. for $C_{84}H_{43}N_6O_7$ 1247.31877 [M + H]$^+$; found 1247.31922.

Supporting Information (see footnote on the first page of this article): Experimental details and spectroscopic data for **13**–**37**, ^{1}H and ^{13}C NMR spectra of **2**–**12**, **19**, **21**, **23**, **25**, **29**, **31**, **33**, **35** and **37**, 2D NMR spectra of fulleropeptide **12** (H,H-COSY, HMBC, HSQC, TOCSY) and table with ^{1}H and ^{13}C NMR chemical shifts for the peptide moieties of fulleropeptides **2**–**12**.

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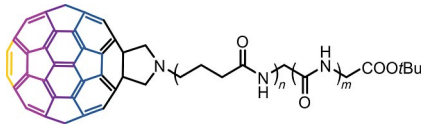
The synthesis of 11 new fulleropeptides Fp-GABA$_n$-Gly$_m$-O*t*Bu (n = 1–3, m = 0–2) containing 4-aminobutyric acid (GABA) and glycyl residues was achieved either by DCC/DMAP-assisted amidation or by [3+2] cycloaddition. In addition, the complete assignment of the peptides' spin systems was accomplished by extensive NMR analysis.



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An Approach to Nanobioparticles – Synthesis and Characterization of Fulleropeptides

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