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## Fulleropyrrolidines with orthogonally flexible substituents – Synthesis and electrochemical properties

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**Abstract:** A large series of disubstituted fulleropyrrolidines was synthesized and analyzed by cyclic voltammetry. The three main groups of target compounds differ by a flexible *N*-chain, while their further diversity was achieved by the introduction of various rigid, aryl substituents at the pyrrolidine carbon. Some dialkyl analogues were also designed for comparison. A standard [3+2]-cycloaddition of *in situ* generated azomethine ylides to C<sub>60</sub> afforded a variety of disubstituted fulleropyrrolidines. Furthermore, a set of dumbbell-shaped di(fulleropyrrolidine) derivatives containing rigid fumaryl or isophthaloyl diamide platform was prepared with the aim of investigating a long-range effect of the second fulleropyrrolidine moiety on their electrochemical properties. All compounds were fully characterized by comparative analysis of spectral data, while examination of electrochemical properties was performed on representative samples, distinguished by main structural subunits. All compounds expressed quite similar electron-accepting ability, lower than C<sub>60</sub>, but higher in comparison to structurally similar *N*-methylfulleropyrrolidine.

**Keywords:** fullerene; cyclic voltammetry; substituents' flexibility.

### INTRODUCTION

Fulleropyrrolidines are a class of fullerene derivatives with a pyrrolidine ring fused to the (6:6) junction of the C<sub>60</sub>. Due to a variety of easily available synthetic precursors, simple preparation, stability under atmospheric conditions,<sup>1–5</sup> as well as suitable physical and chemical properties, they are extensively used in biomedical and materials sciences.<sup>1–5</sup> To the present day, various synthetic protocols for the synthesis of fulleropyrrolidines containing different substituents on the pyrrolidine ring have been developed. One of the most frequent and widely

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accepted method for the synthesis of fulleropyrrolidines is 1,3-dipolar cycloaddition of azomethine ylides to electron deficient fullerene C<sub>60</sub> (Prato reaction).<sup>6,7</sup> Such highly reactive intermediates are usually produced *in situ* by the condensation of  $\alpha$ -amino acids with carbonyl compounds and further decarboxylation of obtained iminium salts.<sup>6,7</sup> Furthermore, other approaches for the preparation of azomethine ylides have been designed, including acid-catalyzed,<sup>8</sup> photochemical<sup>9</sup> or thermal<sup>10</sup> desilylation of trimethylsilyl amino derivatives, tautomerization of imines,<sup>11,12</sup> as well as photochemically-induced reactions of tertiary amines.<sup>13,14</sup> At the same time, variously substituted fulleropyrrolidines have also been prepared utilizing many other methods, such as thermal reactions of aromatic aldehydes and various primary amines,<sup>15,16</sup> thermal and photochemical reactions of  $\alpha$ -amino acids and amino acid esters without an aldehyde,<sup>17,18</sup> reaction of amino acids and quaternary ammonium salts<sup>19</sup> or reaction of halides and  $\alpha$ -amino acids<sup>20</sup> with C<sub>60</sub>. As the first efficient approach for a controlled chiral functionalization of fullerene, Martin and coworkers reported stereo- and enantioselective cycloaddition of  $\alpha$ -iminoesters to C<sub>60</sub>, catalyzed by metal/ligand chiral complexes.<sup>21,22</sup> Thereafter, a stereo controlled, ferric perchlorate-mediated reaction of C<sub>60</sub> with arylmethanamines provided *N*-unsubstituted-2,5-diarylfulleropyrrolidines, easily transformable to trisubstituted analogues.<sup>23</sup>

Great interest in fulleropyrrolidines as promising electron acceptor materials in organic photovoltaic cells (OPCs) has arisen in the recent decade.<sup>5</sup> It was found that the solubility, optical, electrochemical and morphological properties of fulleropyrrolidines played an essential role in achieving the optimal donor-acceptor compatibility and constructing OPCs with upgraded performances.<sup>5</sup> Comprehensive investigations in the field of alternative electron acceptor materials include the study of fulleropyrrolidine analogues of [6,6]-phenyl C<sub>61</sub> butyric acid methyl ester (PC<sub>61</sub>BM), the well-known reference for all kinds of fullerene acceptors in OPCs. Several research groups have synthesized and examined fulleropyrrolidine derivatives containing various aryl, alkyl or polyether groups at the pyrrolidine ring, with similar or better electrochemical and photovoltaic properties compared to those of PC<sub>61</sub>BM under the same conditions.<sup>24–28</sup> All of them have demonstrated that the nature and position of the substituent, electrochemical properties (reflected in the LUMO energy level), and particularly its interactions with the donor polymer had an impact on the solar cell output. Hence, the structural modifications of the substitution pattern, as a method for fine tuning the photovoltaic properties, appeared to be the way for enhancing performances and application of fulleropyrrolidines. Extended research related to fulleropyrrolidines as well as PC<sub>61</sub>BM has been achieved by exploring the influence of *N*-substitution on the optoelectronic, photovoltaic, and morphological properties of the photoactive layer of P3HT/fulleropyrrolidine. It was found that *N*-phenylfulleropyrrolidines expressed a similar reduction pot-

ential, but better miscibility with the polymer donor and higher power conversion efficiency in comparison to *N*-alkyl analogues.<sup>26,29</sup>

These observations complemented with our experience on the chemistry of fulleropyrrolidines inspired us to investigate systematically the influence of the type and position of substituents at the pyrrolidine ring on electrochemical properties of the novel fullerene derivatives. The design of the presented research includes structural variation at two positions of the fulleropyrrolidine core – the pyrrolidine nitrogen and the carbon adjacent to it (C-2) – by moieties of orthogonal flexibility. Beside the spatial orientation at the right angle, the term orthogonally is frequently used to describe independency or quite different properties, as was done here, and can also be found in chromatography, chemistry of protecting groups, or in a new discipline – bio-orthogonal chemistry. Thus, two different aminoalkyl chains (C6 and C10), as well as more soluble long amino-trioxa-alkyl moieties were chosen as flexible *N*-substituents, while rigid aromatic fragments containing both electron-accepting and electron-donating groups were introduced at the C-2 position. Furthermore, one compound with only flexible substituents (C6 and C9 at the pyrrolidine *N* and C-2, respectively) was selected for comparison and introduction in more complex structures in which the rigid segment was located far from fulleropyrrolidine. Finally, constructing dumbbell-like architectures by connecting designed monoadducts *via* two different rigid diamide platforms (fumaryl and isophthaloyl) gave the possibility to investigate a long-range influence of the second fulleropyrrolidine on the electrochemical properties of the compounds. In addition, such well-defined complex structure with subunits suitable to induce self-assembly by different non-covalent interactions ( $\pi$ - $\pi$  of the fullerene core and diamide H-bonds) could be a valuable substrate in the field of supramolecular chemistry.

In aim to broaden the cluster of fulleropyrrolidine based candidates for OPCs, herein the synthesis and electrochemical properties of new sets of mono- and di-fulleropyrrolidines functionalized by alkyl, polyether, aromatic and diamide structural segments are reported. Furthermore, to evaluate preliminary their applicability in OPCs, corresponding LUMO energy levels are also calculated.

## EXPERIMENTAL

### *General*

1,6-Diaminohexane, 1,10-diaminodecane, 1,13-diamino-4,7,10-trioxatridecane, di-*tert*-butyl dicarbonate, benzyl bromoacetate, paraformaldehyde, decanal, benzaldehyde, methoxy- and nitrobenzaldehyde isomers, fumaryl chloride, and isophthaloyl chloride were purchased from Sigma Aldrich and used without further purification. Flash column chromatography (FCC) and dry-column flash chromatography (DCFC) were performed with Merck silica gel 0.04–0.063 and 0.015–0.04 mm, respectively. Thin layer chromatography (TLC) was carried out on precoated silica gel 60 F<sub>254</sub> plates. The IR spectra were recorded with a Perkin-Elmer FTIR 1725X spectrophotometer. The UV spectra were recorded with a GBC Cintra 40 UV–Vis spectrophotometer. <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were recorded with Varian Gemini 200

( $^1\text{H}$  at 200 MHz,  $^{13}\text{C}$  at 50 MHz) and Bruker Avance spectrometers ( $^1\text{H}$  at 500 MHz,  $^{13}\text{C}$  at 125 MHz). Chemical shifts ( $\delta$ ) are expressed in ppm and coupling constants ( $J$ ) in Hz. TMS was used as an internal reference. The sample was dissolved in the indicated solvent system. The homonuclear 2D (DQF-COSY) and the heteronuclear 2D  $^1\text{H}$ - $^{13}\text{C}$  spectra (HSQC, HMBC) were recorded with the usual settings. High-resolution mass spectra (HRMS) were obtained using positive electrospray ionization techniques (ESI) recorded on Bruker-ESI TOF, Agilent Technologies 6210 TOF LC-MS, and LTQ Orbitrap XL instruments. Pyrrolidinic H and C were labeled as  $\text{HC}_{\text{pyrr}}$ . Atoms belonging to the fullerene moiety were written without any label. The H and C atoms of the  $\text{R}^1$  and  $\text{R}^2$  moieties are numbered starting from the pyrrolidine ring. The C atoms of nonyl-group, presented as  $\text{C}'$ , are numbered starting from the pyrrolidine ring.

Analytical and spectral data are given in the Supplementary material to this paper.

#### *Electrochemical measurements*

The electrochemical behavior of  $\text{C}_{60}$  derivatives was investigated using 1 mM solutions of the tested compounds in a dry and degassed mixture ODCB/DMF 2:1 containing 0.1 M TBAP as a supporting electrolyte. To remove oxygen from the electrolyte, the system was bubbled with argon prior to each experiment and an argon atmosphere above the liquid surface was maintained during the scans. The electrochemical measurements were carried out on CH1760b Electrochemical workstation potentiostat (CH Instruments, Austin, TX, USA) using a conventional three-electrode cell (5 mL) equipped with a GCE (glassy carbon electrode) as the working,  $\text{Ag}/\text{Ag}^+$  (a silver wire in contact with 0.01 M  $\text{AgNO}_3$  and 0.10 M TBAP in acetonitrile) as the reference, and a platinum wire as the auxiliary electrode, calibrated with a ferrocene/ferrocenyl couple ( $\text{Fc}/\text{Fc}^+$ ) as an internal standard. All experiments were performed at room temperature in the potential range of  $-2.5$  to  $0.5$  V vs.  $\text{Ag}/\text{Ag}^+$  (*i.e.*  $-2.9$  to  $0.1$  V vs.  $\text{Fc}/\text{Fc}^+$ ), at sweep rates between 0.01 and 0.1 V/s. All half-wave reduction potentials are presented in V vs.  $\text{Fc}/\text{Fc}^+$  (measured  $E_{1/2}$  of  $\text{Fc}/\text{Fc}^+$ :  $0.411$  V vs.  $\text{Ag}/\text{Ag}^+$  in ODCB/DMF 2:1).

Mono-protection of diamines **1** was accomplished by a published methodology.<sup>30</sup> Compounds **2a**,<sup>31</sup> **2b**,<sup>31</sup> **2c**,<sup>32</sup> **3a**,<sup>31</sup> **3b**,<sup>31</sup> **3c**,<sup>33</sup> **4a**,<sup>31</sup> **4b**,<sup>31</sup> **4c**<sup>33</sup> and **5a**<sup>31</sup> were prepared according to published procedures.

#### *General procedure for the synthesis of fulleropyrrolodine monoadducts 6–18*

A suspension of  $\text{C}_{60}$  (0.1 mmol), the corresponding amino acid **4a–c** (0.1 mmol) and an appropriate aldehyde ( $\approx 0.5$  mmol) in PhMe (70–80 mL) was heated at reflux and the solvent was then evaporated to dryness. The residue was purified by dry column flash chromatography (DCFC) on  $\text{SiO}_2$  using listed gradients of solvents as eluents. The first fraction was unconsumed  $\text{C}_{60}$  and the second one afforded the monoadduct. Subsequent precipitation from a concentrated  $\text{CH}_2\text{Cl}_2$  solution with MeOH gave the pure fulleropyrrolidine derivatives (**6–18**, with the exception of 2-nitrophenyl derivative **16c**), as brown powders.

#### *General procedure for the synthesis of di(fulleropyrrolodine)diamides 19–26*

*a) N-Boc-deprotection.* A solution of *N*-Boc protected derivative (**5a**, **7a** or **11c–15c**, 0.1 mmol) in TFA/DCM mixture (1:1, 10–12 mL) was stirred at room temperature for 24 h and evaporated to dryness. The excess of TFA was removed by coevaporation with PhMe ( $3 \times 10$  mL), giving the corresponding TFA salt in quantitative yield, which was used without purification for further coupling;

*b) Coupling of fullerene monoadduct with fumaryl chloride or isophthaloyl chloride.* To a solution of the corresponding TFA salt (0.1 mmol) in 30 mL of  $\text{CH}_2\text{Cl}_2$  was added 2 mL of pyridine, the mixture was stirred for 20 min at room temperature, and then DMAP (0.3 mmol)

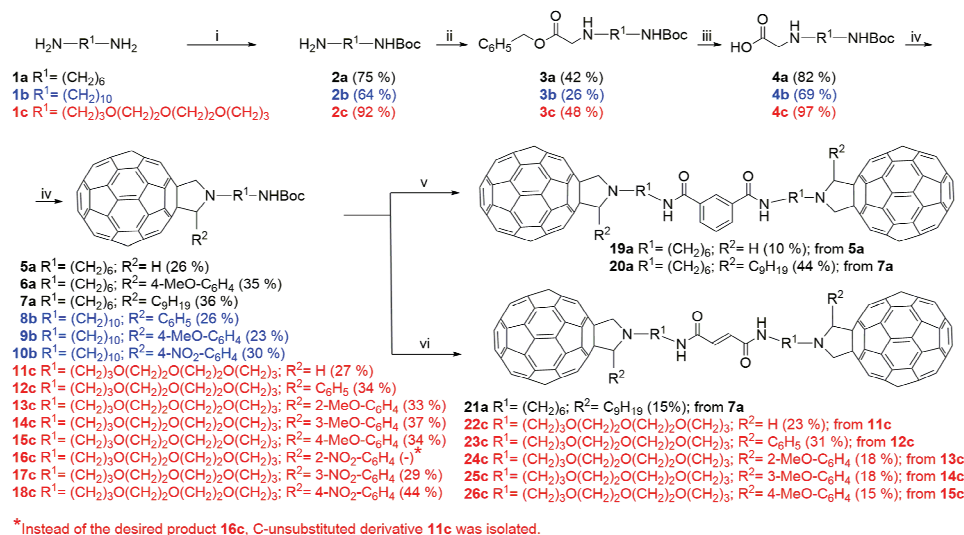
was introduced and the mixture was stirred for an additional 15 min at room temperature. After addition of fumaryl chloride or isophthaloyl chloride (0.05 mmol), the mixture was left to stir for 48 h at room temperature. The solvent was evaporated, and the residue was purified by flash column chromatography (FCC) on SiO<sub>2</sub>, with use of the eluents listed below. Subsequent precipitation from CHCl<sub>3</sub> solution with MeOH gave the pure fulleropyrrolidine diamides (**19–26**), as brown powders.

## RESULTS AND DISCUSSION

### Synthesis

Three principal series of target fulleropyrrolidines differing by long, flexible pyrrolidine *N*-substituents were designed. To this purpose, alkylamino and polyoxaalkylamino side chains containing hexamethylene, decamethylene and trioxatridecane units were chosen (**a**, **b** and **c**-series of compounds, respectively, Scheme 1). Furthermore, rigid aromatic subunits with variously positioned electron-donating (OMe) and electron-accepting (NO<sub>2</sub>) groups, and more soluble alkyl-segment (C9) were employed as pyrrolidine C-2 substituents. In addition, corresponding 2-phenyl and 2-unsubstituted analogues were designed as referent compounds. Finally, two rigid platforms, built of isophthaloyl- and fumaryl-diamide moieties were used for the construction of dumbbell-like difulleropyrrolidines.

Following the described strategy, target compounds were synthesized according to Scheme 1. A standard three-step procedure, consisting of the Boc-monoprotection of commercially available diamines **1**, mono-alkylation of their non-protected amino group by benzyl bromoacetate (BBA) and Pd/C catalyzed hydrogenolysis of obtained benzyl esters **3**, provided *N*-derivatized glycines **4** in satisfactory yields (overall 11–42 %). Utilizing the well-known Prato method<sup>1,2,6</sup> based on the 1,3-dipolar cyclo-addition of azomethine ylides to C<sub>60</sub>, the obtained acids **4** were treated with fullerene and nine commercially available aldehydes (formaldehyde, decanal, benzaldehyde, nitro- and methoxy benzaldehydes) in refluxing toluene. Easily accomplished purification by dry column flash chromatography on SiO<sub>2</sub> afforded a series of fulleropyrrolidines **5–18** in expected yields (23–44 %), except for the lack of the expected 2-nitrophenyl derivative **16c**. Unusually, the reaction with *o*-nitrobenzaldehyde afforded 2-unsubstituted fulleropyrrolidine **11c** (11 %) as the only product (Supplementary material, Fig. S-61). Since Zhang *et al.*<sup>34,35</sup> have reported the successful preparation and characterization of all three isomeric 2-(nitrophenyl)fulleropyrrolidine derivatives by the Prato cycloaddition reaction with sarcosine, an attempt was made to synthesize derivative **16c** under their reaction conditions, but again only product **11c** was obtained. At the same time, the finding was in accordance with the published degradation of 2-nitrobenzaldehyde to formaldehyde *via* 1,7-electrocyclization of the corresponding ylide to the adjacent nitro-group, observed in reactions with non-fullerene dipolarophiles.<sup>36</sup>



Scheme 1. Synthetic route towards C<sub>60</sub> fulleropyrrolidine derivatives **5-26** starting from diamines **1a-c**: *i*) Boc<sub>2</sub>O, CHCl<sub>3</sub>, 0 °C → r.t., 24 h; *ii*) BBA, CH<sub>2</sub>Cl<sub>2</sub>, 0 °C → r.t., 24 h; *iii*) H<sub>2</sub>, Pd/C, MeOH, r.t., 2 h; *iv*) C<sub>60</sub>, R<sup>2</sup>-CHO, PhMe, reflux; *v*) (a) **5a** or **7a**, TFA/CH<sub>2</sub>Cl<sub>2</sub>, r.t., 24 h; (b) isophthaloyl-chloride, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, Py/ODCB, r.t., 48 h; *vi*) (a) **7a** or **11c-15c**, TFA/CH<sub>2</sub>Cl<sub>2</sub>, r.t., 24 h; (b) fumaryl-chloride, DMAP, CH<sub>2</sub>Cl<sub>2</sub>, Py, r.t., 48 h.

To prepare more complex derivatives – di(fulleropyrrolidines), some of synthesized compounds were used as precursors, since *N*-Boc protected fulleropyrrolidine amines represent good precursors for amide coupling with appropriate diacids (platforms). The TFA-mediated deprotection in dichloromethane provided almost quantitatively corresponding TFA-salts, which were further transformed to difullerene derivatives by coupling with isophthaloyl or fumaryl dichloride in the presence of DMAP and pyridine. To examine the influence of changes in the platform flexibility on the properties of the compound, the monoadduct **7a** was coupled to both the rigid isophthaloyl and slightly more flexible fumaryl-platform, providing di(fulleropyrrolidines) **20a** and **21a**, respectively. In addition, monoadduct **5a**, with unsubstituted C-2 position, was also transformed to difullerene derivative **19a**, but extremely low solubility disabled its full characterization. Consequently, compound **19a**, characterized only by the <sup>1</sup>H-NMR and IR spectra, was not used for further studies. In the other cases, the structure of the platform was chosen by complementarity with the C-2 substituent, *i.e.*, more flexible fumaric acid served to link fulleropyrrolidines with rigid, aromatic segment at pyrrolidine C-2. So, utilizing monoadducts **11c** and **12c** (with H and Ph moieties at C-2) as model compounds, as well as **13c-15c** (2-, 3-, and 4-methoxyphenyl moieties at C-2), difullerenes **22c-26c** were obtained in yields varying from 15 to 31 % (Scheme 1).

### Structure determination

The structures of the known compounds **2–5** were confirmed by comparison with literature data (see Supplementary material). As was mentioned before, the poorly soluble compound **19a** was characterized only by its  $^1\text{H-NMR}$  and IR spectra. In addition, compounds **20a** and **21a** expressed extremely low ionizability/solubility under the applied conditions, so neither ESI-TOF, nor HESI Orbitrap provided satisfactory mass spectra. The structures of all other synthesized fullerene compounds were characterized in detail by high-resolution mass spectrometry (HRMS), FT-IR, UV-Vis, 1D ( $^1\text{H-NMR}$  and  $^{13}\text{C-NMR}$ ) and 2D NMR spectra (COSY, HSQC and HMBC, Supplementary material). The correct positive ionization peak was observed in ESI-TOF and HESI Orbitrap mass spectra for all ionizable fulleropyrrolidines, while the UV-Vis spectra showed a characteristic peak in the range of 431–433 nm, typical for [6,6]-mono-adducts of  $\text{C}_{60}$ .

All peaks belonging to substituted fulleropyrrolidine moieties were observed in the corresponding NMR spectra. The characteristic  $^1\text{H}/^{13}\text{C-NMR}$  signals of all the new synthesized fullerene derivatives are given in Tables S-I–S-III). As representative examples, the  $^1\text{H-NMR}$  spectra of the monosubstituted fulleropyrrolidine **11c**, the disubstituted 2-phenyl- (**12c**) and the isomeric 2-(methoxyphenyl)-3,4-fulleropyrrolidines (**13c–15c**), as well as the corresponding difullerene diamides **22c–26c** synthesized from them are presented in Figs. 1 and 2, respectively. Unlike the characteristic fulleropyrrolidine  $^1\text{H}$  singlet at  $\delta$  4.4 ppm for C-unsubstituted fulleropyrrolidine **11c**, the  $^1\text{H-NMR}$  spectra of the newly synthesized disubstituted  $\text{C}_{60}$  derivatives contained the expected multiplication of the signals. Thus, the pyrrolidine proton attached to the chiral C-2, gave a singlet in a narrow  $\delta$  range of 5.0–5.7 ppm ( $\text{R}^2$ - aryl) or a triplet at  $\delta = 4.13$  ppm ( $\text{R}^2$ -nonyl). At the same time, two diastereotopic protons at pyrrolidine C-5 responded as two doublets in a wide  $\delta$  range of 4.10–5.14 ppm, with a coupling constant of 10 Hz.

Except for the 2-(2-methoxyphenyl)-substituted derivatives **13c** and **24c**, the other 2-arylfulleropyrrolidines displayed a broadening of the *ortho*-H ( $\text{HC}_{\text{ar}}(2',6')$ ) singlet in the  $\delta$  range of 7.3–8.7 ppm, indicating the restricted rotation of the phenyl group on the pyrrolidine ring in the case of *ortho*-substituted derivatives, as well as the fast exchange between *ortho*-H in the others.<sup>37,38</sup> In addition, the remaining aromatic protons gave the usual phenyl signal pattern, located in the  $\delta$  zone of 6.8–8.7 ppm (Figs. 1 and 2, and Tables S-I–S-III). Due to distinct chemical environments, the methylene protons adjacent to pyrrolidine nitrogen ( $\text{CH}_2(1)$ ) appeared as two sets of quite distant multiplets ( $\Delta\delta = 0.5$ –1 ppm, Figs. 1 and 2), which is in good agreement with other reported *N*-(alkyl)pyrrolidino-fullerenes.<sup>39</sup> The presence of the *N-tert*-butoxycarbonyl protecting group ( $\text{NH-COOC}(\text{CH}_3)_3$ )

was confirmed by two singlets – a broad one in the  $\delta$  range of 4.5–5.0 ppm attributable to the carbamate proton, and one at  $\delta \approx 1.5$  ppm assigned to the CH<sub>3</sub> group.

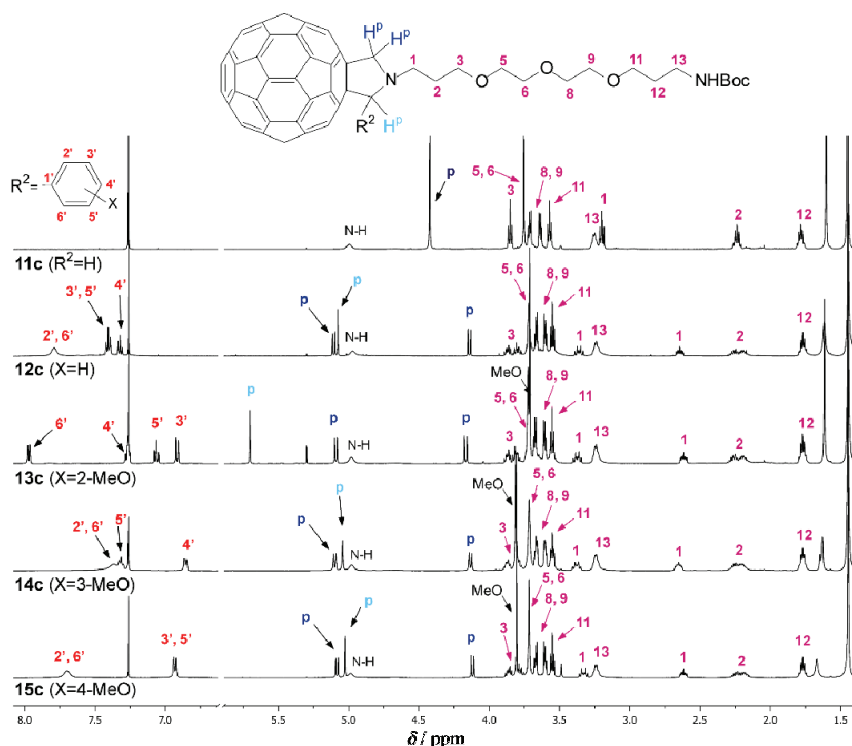


Fig. 1. Comparison of the <sup>1</sup>H-NMR spectra of monosubstituted fulleropyrrolidine **11c** and disubstituted fulleropyrrolidines **12c–15c**.

In accordance with the *C*<sub>1</sub> symmetry of mono- fulleropyrrolidines, the 58 sp<sup>2</sup> carbons of the fullerene moiety resonated in all cases in the same region ( $\delta$  135–157 ppm) giving a similar number of signals (at least 43). Two peaks in narrow  $\delta$  ranges of 77.1–76.1 and 70.8–68.8 ppm, attributable to two sp<sup>3</sup> C of the fullerene subunit confirmed the 6,6-ring junction of the C<sub>60</sub> to the pyrrolidine ring. In addition, the pyrrolidine methine carbon bearing an aromatic or the nonyl group resonates at  $\delta \approx 82$  and 77 ppm, respectively, except for 2-MeO-C<sub>6</sub>H<sub>4</sub>-derivatives **13c** and **24c** ( $\delta \approx 74$  ppm), whereas the pyrrolidine methylene carbon in all cases appeared at  $\delta \approx 67$  ppm. Moreover, the *N*-Boc segment resonated at  $\delta$  156 (C=O), 79 (C) and 28.5 ppm (CH<sub>3</sub>). Besides the disappearance of the <sup>1</sup>H- and <sup>13</sup>C-signals belonging to the *N*-Boc group, the NMR spectra of difullerene compounds **21a**, **22c–26c** showed the expected signals corresponding to the fumaramide CO bond at  $\delta \approx 165$  ppm, the fumaramide double bond signals at about  $\delta$  6.8 ppm/133 ppm, as well as an exchangeable amide NH proton in the  $\delta$  range of



6.9–8.0 ppm (Fig. 2, Table S-III). In addition, the characteristic peaks of the isophthaloyl diamide moiety in difullerenes **19a** and **20a** were located in their  $^1\text{H}$ -NMR spectra at  $\delta$  6.3 (amide NH), 8.2 (H(2)), 7.9 (H(4,6)) and 7.5 ppm (H(5)), as well as in the  $^{13}\text{C}$ -NMR spectrum of **20a** at  $\delta$  166.6, 135.1, 125.3, 129.7 and 129.0 ppm for amide CO, aryl C(1,3), C(2), C(4,6) and C(5), respectively (Table S-III). Additionally, the  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra of all the prepared derivatives revealed the presence of the signals of aliphatic protons and carbons belonging to the  $\text{R}^1$  and  $\text{R}^2$  methylene and methyl groups on the pyrrolidine ring (Figs. 1 and 2, Tables S-I–S-III).

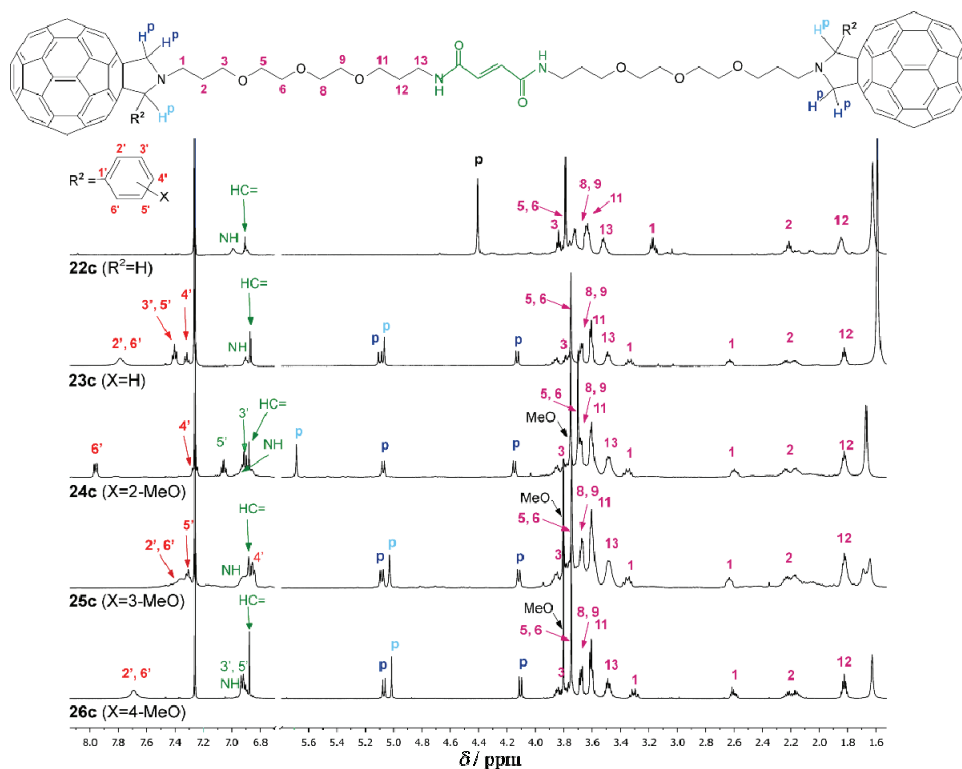


Fig. 2. Comparison of the  $^1\text{H}$ -NMR spectra of difulleropyrrolidine diamides **22c–26c**.

### Electrochemical properties

The redox properties of fullerene derivatives, as well as the possibility of intermolecular electronic communication between their segments were studied by the cyclic voltammetry (CV). To these purposes, a set of 12 representative compounds, differing in the number of the fullerene subunits, structure of the central rigid platform in difullerene compounds, and *N*- and *C*-pyrrolidine substituents was selected. In addition, the  $\text{C}_{60}$  and *N*-methylfulleropyrrolidine (NMFP) were

used as referent compounds. The CV curves of tested samples were recorded in an ODCB / DMF (2:1) mixture at different scan rates, varying from 50 to 200  $\text{mV s}^{-1}$ . At higher scan rates, voltammograms with broad end, low separated peaks were obtained, while better electrochemical response was achieved only at the lowest scan rate of 50  $\text{mV s}^{-1}$ . Under such conditions, all tested samples gave a uniform electrochemical response consisting of three redox waves attributable to three successive reversible redox processes on the fullerene cage (Fig. 3). Their half-potentials were in a quite narrow interspace of 40 mV. Thus, the first reduction occurred in the range from  $-1.02$  to  $-1.06$  V vs.  $\text{Fc}/\text{Fc}^+$ , the second from  $-1.44$  to  $-1.48$  V vs.  $\text{Fc}/\text{Fc}^+$ , and the third one at  $E_{1/2} = -2.06 - -2.10$  V vs.  $\text{Fc}/\text{Fc}^+$  (Table I). As can be seen from Table I and Fig. 4, the number of fullerene subunits had no influence on electrochemical behavior of derivatives (**7a** vs. **20a** or **21a**, **12c** vs. **23c** and **13c** vs. **24c**). The same effect was observed by varying the structure of the central rigid platform in difullerene compounds (**20a** vs. **21a**). Further, an almost identical electron accepting ability was observed in monofullerenes regardless of the presence *N*-alkyl or trioxa tether (**6a** vs. **9b** vs. **15c**, **8b** vs. **12c**), as well as C-alkyl, phenyl or isomeric methoxyphenyl substituted pyrrolidine subunits (**12c** vs. **13c** vs. **14c** vs. **15c**, **6a** vs. **7a** and **8b** vs. **9b**). In addition, no electronic communications between fullerene subunits in difullerene compounds were observed, since redox processes proceeded simultaneously, affording the same half-potential values for both carbon spheres. The absence of interfullerene interactions in the ground state was also found in other dumbbell-derivatives,<sup>40,41</sup> with the exception of difullerenes connected directly *via* oxygen<sup>42</sup> or a metal.<sup>43–45</sup>

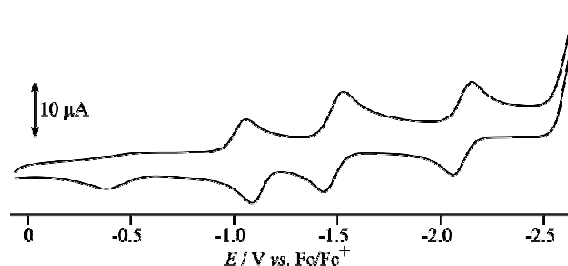


Fig. 3. A representative CV voltammogram (compound **6a**).

All tested compounds expressed the expected, slightly aggravated electron affinity of the fullerene subunit upon functionalization, reflected in the negatively shifted potentials in comparison to pristine  $\text{C}_{60}$  (Fig. 4). However, less disruption of the  $\pi$ -electronic system than in the referent NMFP was observed. Consequently, the corresponding LUMO energy levels were also negatively shifted by 140–180 eV in comparison to pristine  $\text{C}_{60}$ , but in the same range, more positive relative to NMFP (120–160 eV, Fig. 4).

TABLE I. Half-wave reduction potentials and the LUMO energy levels of selected compounds in ODCB/DMF (2:1) at a scan rate of 50 mV

Run	Compound	$E_{1/2} / \text{V}$			$E_{\text{LUMO}}^a / \text{eV}$
		I	II	III	
1	$\text{C}_{60}$ <sup>a</sup>	-0.88	-1.34	-1.88	-5.68
2	<b>6a</b>	-1.04	-1.46	-2.08	-5.84
3	<b>7a</b>	-1.02	-1.46	-2.10	-5.82
4	<b>8b</b>	-1.04	-1.45	-2.09	-5.84
5	<b>9b</b>	-1.04	-1.46	-2.08	-5.84
6	<b>12c</b>	-1.04	-1.46	-2.08	-5.84
7	<b>13c</b>	-1.06	-1.46	-2.10	-5.86
8	<b>14c</b>	-1.04	-1.48	-2.08	-5.84
9	<b>15c</b>	-1.04	-1.46	-2.08	-5.84
10	<b>20a</b>	-1.04	-1.44	-2.10	-5.84
11	<b>21a</b>	-1.06	-1.46	-2.08	-5.86
12	<b>23c</b>	-1.06	-1.45	-2.06	-5.86
13	<b>24c</b>	-1.05	-1.48	-2.10	-5.85
14	NMFP	-1.14	-1.54	-2.16	-5.94

<sup>a</sup> $E_{\text{LUMO}} = -4.80 + E_{1/2}$ ; <sup>b</sup>the only compound that showed four reduction waves, with  $E_{1/2}(\text{IV}) = -2.42 \text{ V}$

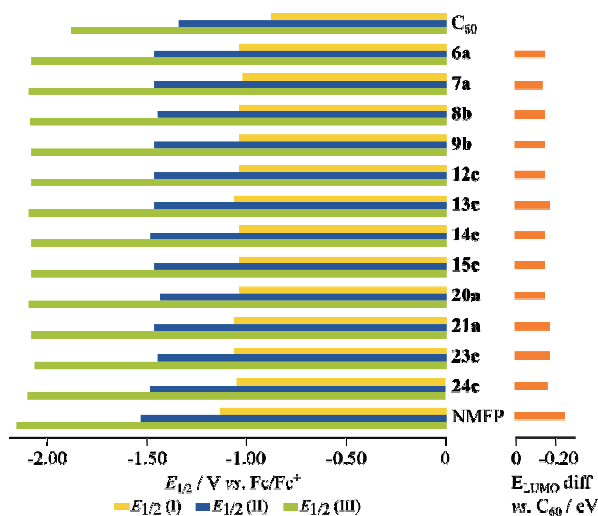


Fig. 4. Distribution of half-wave potentials of tested compounds and their LUMO energy levels relative to those of  $\text{C}_{60}$ .

Furthermore, analysis of obtained voltammograms pointed to a strong adsorption on the electrode surface, since almost negligible separation of anodic and cathodic peaks of the first reduction/reoxidation in majority of compounds (9 out of 12) was found.<sup>46</sup> Additionally, the multiplication of signals in some samples (4 out of 12) varying from small shoulders to a clearly doubled waves indicated the presence of both adsorbed and dissolved species.<sup>46</sup>

Finally, no linear correlation between the peak current and the scan rate, nor its square root value was found in any compound, implying a mutual contribution of diffusion and absorption controlled redox processes.

#### CONCLUSIONS

To understand more in detail the effect of the pyrrolidine substitution on the electrochemical properties of fulleropyrrolidines, as well as to expand the spectrum of fulleropyrrolidine OPCs candidates, a group of new compounds was designed, synthesized and studied by cyclic voltammetry. The impact of alteration of the structural segments at the pyrrolidine carbon and nitrogen was investigated by the introduction of linear and different aromatic substituents at pyrrolidine C-2, as well as various flexible side chains at nitrogen. In addition, to study the long-range effect of the second fullerene moiety on the electrochemical properties of the compounds, a corresponding dumbbell-like framework was designed by bridging two fulleropyrrolidine units *via* different rigid, diamide platforms. Following a simple synthetic pathway, a variety of new compounds was obtained and fully characterized by means of spectral data. In almost all cases, the expected compounds were formed in satisfactory yields. The only deviation was observed in the reaction with 2-nitrobenzaldehyde, which afforded exclusively C-unfunctionalized fulleropyrrolidine despite a published preparation of such a product. Nevertheless, an indirect formation of formaldehyde as reactive species agreed with the published degradation of 2-nitrobenzaldehyde to formaldehyde in the presence of non-fullerene dipolarophiles. Cyclic voltammetry experiments, performed on selected compounds differing in main structural subunits, revealed their highly uniform electrochemical behavior, regardless of the nature of the substituents. All samples expressed lower electron-accepting ability, and consequently lower LUMO energy level than the unfunctionalized C<sub>60</sub>. On the other hand, they showed more favorable electrochemical properties in comparison to the structurally more similar referent compound *N*-methylfulleropyrrolidine. In addition, a strong adsorption of majority of compounds on the electrode surface made them suitable for further research oriented towards the design of electrodes with upgraded sensitivity.

#### SUPPLEMENTARY MATERIAL

Additional data and information, containing experimental details, tabular representation of the NMR data of compounds **6–26**, copies of their HRMS, <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, COSY and HMBC spectra, and the CV curves of all tested compounds, are available electronically at the pages of journal website: <https://www.shd-pub.org.rs/index.php/JSCS/article/view/10935>, or from the corresponding author on request.

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ИЗВОД  
ФУЛЕРОПИРОЛИДИНИ СА ОРТОГОНАЛНО ФЛЕКСИБИЛНИМ СУПСТИТУЕНТИМА –  
СИНТЕЗА И ЕЛЕКТРОХЕМИЈСКЕ ОСОБИНЕ

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Велика серија дисупституисаних фулеропиролидина је синтетисана и анализирана цикличном волтаметријом. Три главне групе циљних једињења разликују се по флексибилном бочном низу на атому азота, а додатна диверсификација постигнута је увођењем различитих крутих, арил-супституената на пиролидинском атому угљеника. За поређење су синтетисани и одређени диалкил-аналози. Сет дисупституисаних фулеропиролидина добијен је стандардном [3+2]-циклоадицијом ин ситу генерисаних азометинских илида на C<sub>60</sub>. Осим тога, у циљу испитивања даљинског утицаја фулеропиролидинске структуре на електрохемијске особине, синтетисани су и дифулеренски деривати код којих су терминално позициониране фулеренске подјединице премошћене фумарилном или изофталоилном крутом платформом. Сва једињења су у потпуности окарактерисана упоредном анализом спектралних података, док је сет одабраних једињења, са разликама у главним структурним подјединицама, искоришћен за испитивање електрохемијских особина. Сва испитивана једињења показала су врло сличну способност прихватања електрона, нижу у односу на C<sub>60</sub>, а вишу од структурно сличног N-метилфулеропиролидина.

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